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13. ABSTRACT *(Maximum 200 words)*

THE PURPOSE OF THE SAMPLING AND CHEMICAL ANALYSIS QUALITY ASSURANCE PROGRAM IS TO ESTABLISH AND MAINTAIN LABORATORY PRACTICES TO ENSURE THE SCIENTIFIC RELIABILITY AND COMPATIBILITY OF LABORATORY DATA GENERATED IN SUPPORT OF THE USATHAMA PROGRAMS. THIS DOCUMENT OUTLINES THE PURPOSE, POLICIES, ORGANIZATION, AND OPERATIONS ESTABLISHED TO SUPPORT THE CHEMICAL ANALYSES CONDUCTED FOR USATHAMA.

THE SPECIFIC OBJECTIVES OF THE QA PROGRAM ARE TO:

1. ESTIMATE THE LEVEL OF QUALITY OF EACH ANALYTICAL SYSTEM
2. ASSIST IN THE EARLY RECOGNITION OF DEFICIENCIES
3. ENABLE THE FIELD LABORATORY TO TAKE THAT ACTION WHICH IS NECESSARY TO ENSURE THE VALIDITY OF DATA
4. REQUIRE SUFFICIENT DOCUMENTATION TO VERIFY THE CREDIBILITY OF THE QUALITY OF DATA.

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SAMPLING AND CHEMICAL ANALYSIS QUALITY ASSURANCE PROGRAM FOR US ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY (USATHAMA)

US ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

87048R03

SAMPLING AND CHEMICAL ANALYSIS QUALITY ASSURANCE PROGRAM FOR US ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY (USATHAMA)

APRIL 1982

DEPARTMENT OF THE ARMY
US ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
ABERDEEN PROVING GROUND, MD 21010

The USATHAMA Quality Assurance Program is a guidance document to be used by a performer in preparing a Quality Control Plan.

The Quality Control Plan submitted in fulfillment of the proposed Scope of Work should be a detailed, step-by-step document implementing the procedures described herewithin.

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I. PURPOSE OF THE QUALITY ASSURANCE PROGRAM

The purpose of the Sampling and Chemical Analysis Quality Assurance (QA) Program is to establish and maintain laboratory practices to ensure the scientific reliability and compatibility of laboratory data generated in support of the US Army Toxic and Hazardous Materials Agency (USATHAMA) programs.

II. INTRODUCTION

This Quality Assurance (QA) Program outlines the purpose, policies, organization and operations established to support the chemical analyses conducted for USATHAMA. Implementation of this program at all laboratories performing chemical analyses for USATHAMA programs will better ensure the validity of data and provide a reliable foundation on which to base decisions.

The concepts expressed in this document represent what is considered by USATHAMA to be the best approach for conducting chemical analyses. Principles and procedures are a result of considerations of general operations and trends in the field of analytical chemistry and of previous experiences in USATHAMA programs. This QA Program has been designed to be theoretically sound and operationally efficient.

In implementing this Quality Assurance Program, it is important that the reader understand the definitions used herewithin. A Quality Assurance Program is the concepts used in defining a "...system for verifying and maintaining a desired level of quality in a product or process"[1]. A Quality Control Plan is a specific, step-by-step description of how the Quality Assurance Program will be carried out.

Although USATHAMA is sensitive to differences in laboratory practices, it is essential that all products submitted to USATHAMA, for approval, are in the format prescribed in this Quality Assurance Program.

QUALITY ASSURANCE

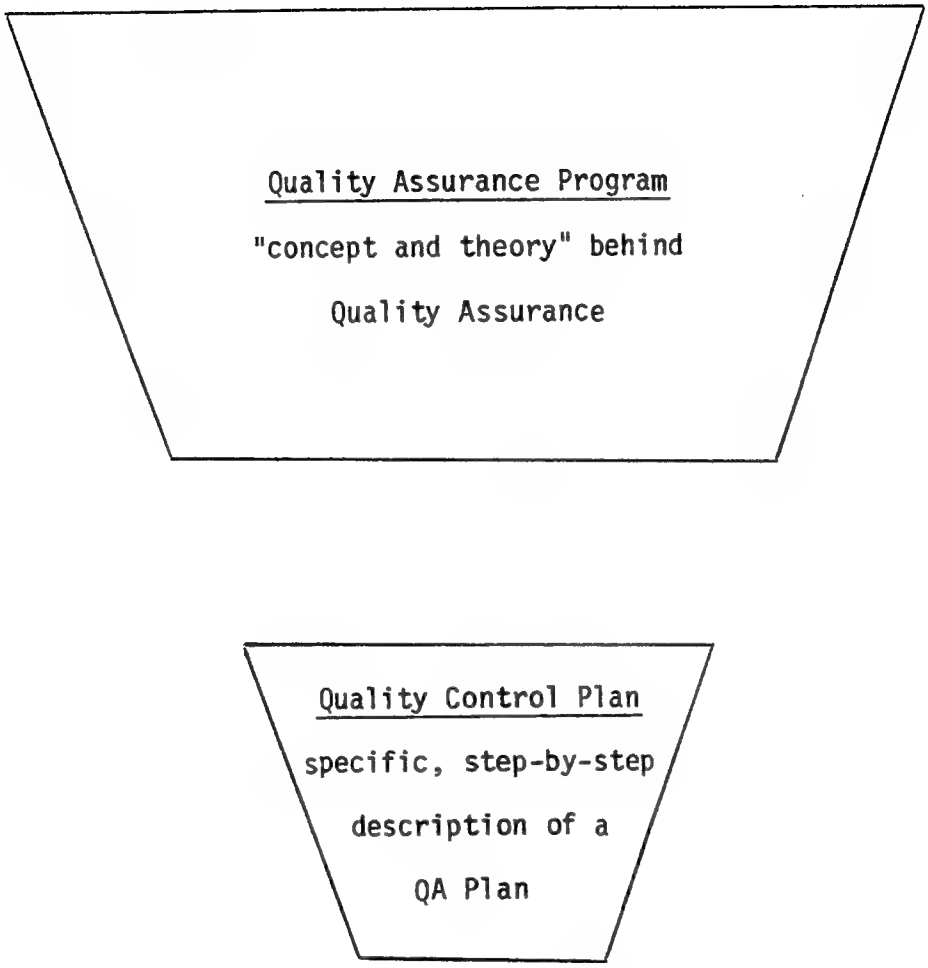


Figure 1.

III. QUALITY ASSURANCE OBJECTIVES

The specific objectives of the Quality Assurance Program are to:

A. Estimate the level of quality of each analytical system without requiring excessive precision, accuracy, and sensitivity.

B. Assist in the early recognition of deficiencies which might affect the quality of data.

C. Enable the field laboratory to take that action which is necessary to ensure the validity of laboratory data.

D. Require sufficient documentation to verify the credibility of the quality of data submitted to USATHAMA.

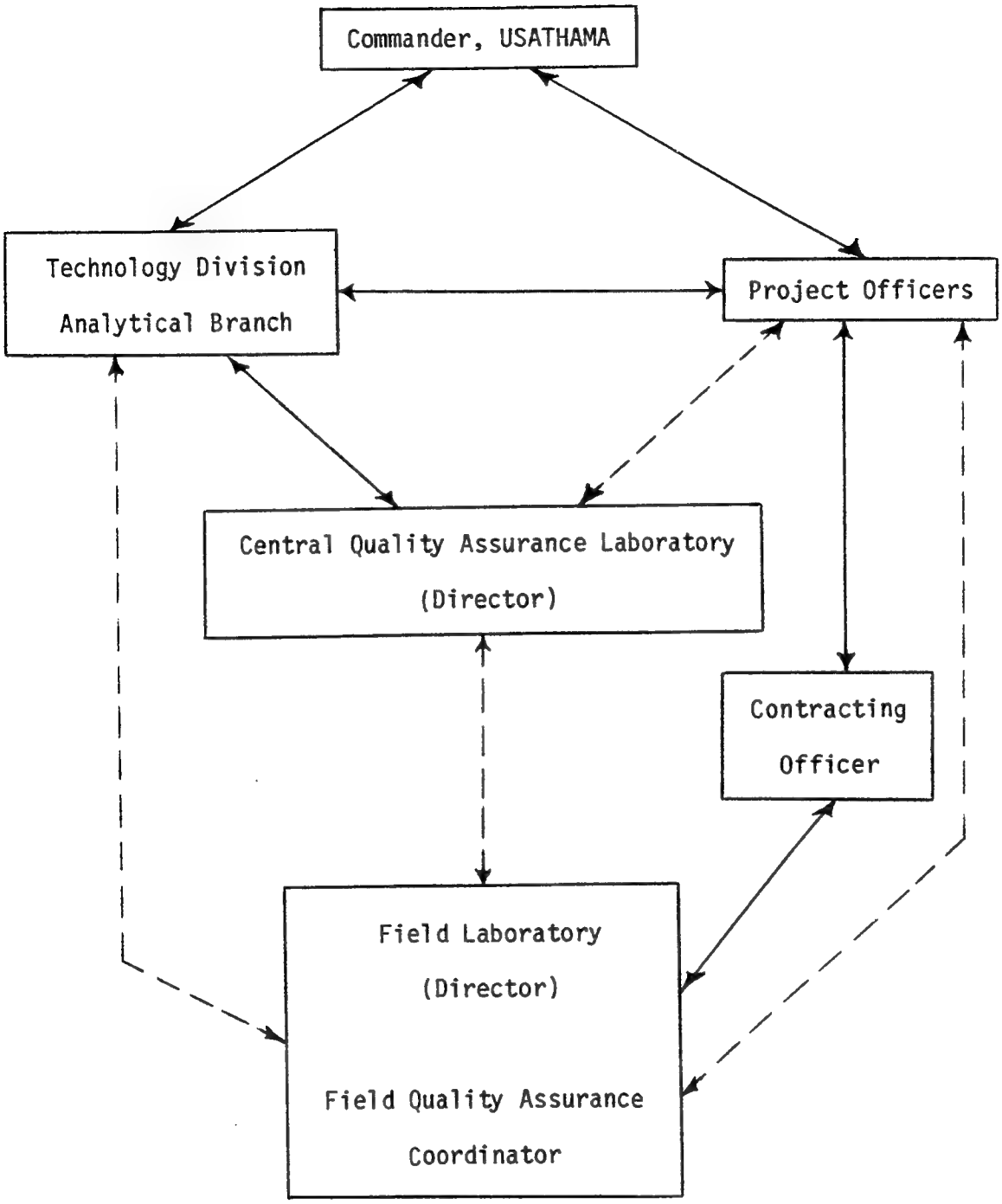
IV. ORGANIZATION OF THE PROGRAM

IV. ORGANIZATION OF THE PROGRAM

A. INTRODUCTION:

The Commander of USATHAMA is ultimately responsible for the quality of data collected in support of USATHAMA's programs. The Commander, through the Analytical Branch and Project Officers, directs the QA Program to adequately document the control of data.

In directing the Quality Assurance Program, USATHAMA adopted a central laboratory - field laboratory concept. The central laboratory is the Central Quality Assurance (QA) Laboratory, with a director serving as the Central Quality Assurance Coordinator. The field laboratories are those laboratories conducting analyses for USATHAMA programs under the direction of the Field Laboratory Director. A Field Quality Assurance Coordinator is appointed by the Field Laboratory Director as an independent reviewer of the Field Laboratory's quality assurance activities.



— Formal Communication

--- Informal Communication

Figure 2.

Organization of USATHAMA Quality Assurance Program

B. RESPONSIBILITIES AND AUTHORITY OF THE US ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY (USATHAMA):

1. Analytical Branch, Technology Division, will:

- Advise the Commander on quality assurance practices.
- Recommend to the Commander quality assurance practices to be used to support USATHAMA programs.
- Provide direction to the Central QA Laboratory.
- Approve the Quality Control Plan submitted by the Field Laboratories.
- Certify Field Laboratory analytical methods prior to the start of field sample analyses.
- Advise project officers on the preparation of analytical and quality control segments of scopes of work.
- Provide guidance to USATHAMA project officers on implementation of quality control in field laboratories.
- Provide guidance to project officers on chemistry matters.
- Evaluate the quality of data generated by field laboratories.

- Monitor the effective implementation of quality control at Field Laboratories and report questionable practices to the Commander.

2. Project Officer will:

- Be the principal contact between USATHAMA and the Field Laboratories.

- Ensure effective implementation of the USATHAMA QA Program.

- Submit requests to the Analytical Branch to supply reference materials to Field Laboratories.

- Inform the Analytical Branch of difficulties and problems encountered by the Field Laboratories in implementing the QA Program.

- Inform the Analytical Branch of changes in approved sampling and analysis procedures.

- Provide Field Laboratory quality control plans to the Analytical Branch for review and approval.

- Provide Field Laboratory certification documentation to the Analytical Branch for review and approval.

- Notify Field Laboratories of certification status.

C. RESPONSIBILITIES AND AUTHORITY OF THE CENTRAL QUALITY ASSURANCE LABORATORY DIRECTOR:

- Serve as the Central Quality Assurance Coordinator (CQAC) for USATHAMA programs through the USATHAMA Analytical Branch.

- Provide technical evaluations of Quality Control (QC) Plans submitted by performers, as required. Quality Control Plans are to be developed according to this USATHAMA Quality Assurance Program.

- Provide technical evaluations of laboratory facilities and capabilities, as required.

- Manage the Quality Assurance activities required for the preparation of standards and the evaluation of methods.

- Maintain the analytical reference material repository.

- Provide analytical reference materials with supporting documentation to Field Laboratories.

- Notify the Field Laboratory Chief, USATHAMA Project Officer, and Analytical Branch when a situation exists at a Field Laboratory that precludes statistical control of results.

- Provide a systematic review of how the USATHAMA Quality Assurance Program is being implemented at each Field Laboratory and report the findings (with any comments from the Field Laboratory) to the USATHAMA Analytical Branch and Project Officer. Such reviews will require visits to the Field Laboratories prior to and during the conduct of analyses.

- On request from the USATHAMA Analytical Branch provide quality control samples and data analysis program tape to field laboratories.

D. RESPONSIBILITIES AND AUTHORITY OF THE FIELD LABORATORY DIRECTOR:

The responsibility for implementation of the USATHAMA Quality Assurance Program resides with the Director or Chief of that laboratory. He will:

- Submit to USATHAMA for approval a detailed Quality Control Plan specific to the USATHAMA program being supported.

- Appoint and support a Field Quality Assurance Coordinator (FQAC) who will not be subordinate to or be in charge of any person having direct responsibility for analyses.

- Request analytical reference materials from USATHAMA through the project officer.

- Ensure that all test and measurement equipment is properly calibrated.

- Submit to USATHAMA the required documented methods and laboratory certification data prior to field sample analysis.

- Be responsible for entering the analytical methods via the terminal, if a terminal is provided on the contract, to the central computer at Edgewood.

E. RESPONSIBILITIES AND AUTHORITY OF THE FIELD QUALITY ASSURANCE COORDINATOR (FQAC):

The FQAC will:

- Monitor the quality assurance activities of the laboratory, ensure conformance with authorized policies, procedures, and sound practices, and recommend improvements as necessary.

- Inform the Field Laboratory management of nonconformance to the QA program.

- Be responsible for the logging in of samples, introduction of control samples into the sample train, and establishment of testing lots.

- Ensure that sampling is conducted in a manner consistent with USATHAMA guidelines.

- Approve all laboratory data before those data are reported or transmitted to permanent storage. When automated data acquisition systems are employed, provision must be made for temporary storage where the results are detained, pending acceptance by the FQAC. Before releasing data, the FQAC must have supporting information such as control charts and other performance indicators to demonstrate that the systems which produced the data were, in fact, in control. Use of automatic data processing/management

systems must not jeopardize the availability of documented calculations for inspection. The FQAC is responsible for the maintenance of these records.

- Maintain an awareness of the entire laboratory operation to detect conditions which might directly or indirectly jeopardize controls of the various analytical systems. Examples: improper calibration of equipment; cross contamination through improper storage of samples.

- Ensure that subsampling and other handling procedures are adequate for the sample types received.

- Oversee the quality of purchased laboratory materials, reagents, and chemicals to ensure that these supplies do not jeopardize the quality of analytical results.

- Maintain a log of certification of analysts in the performance of the required analyses.

V. LABORATORY CERTIFICATION

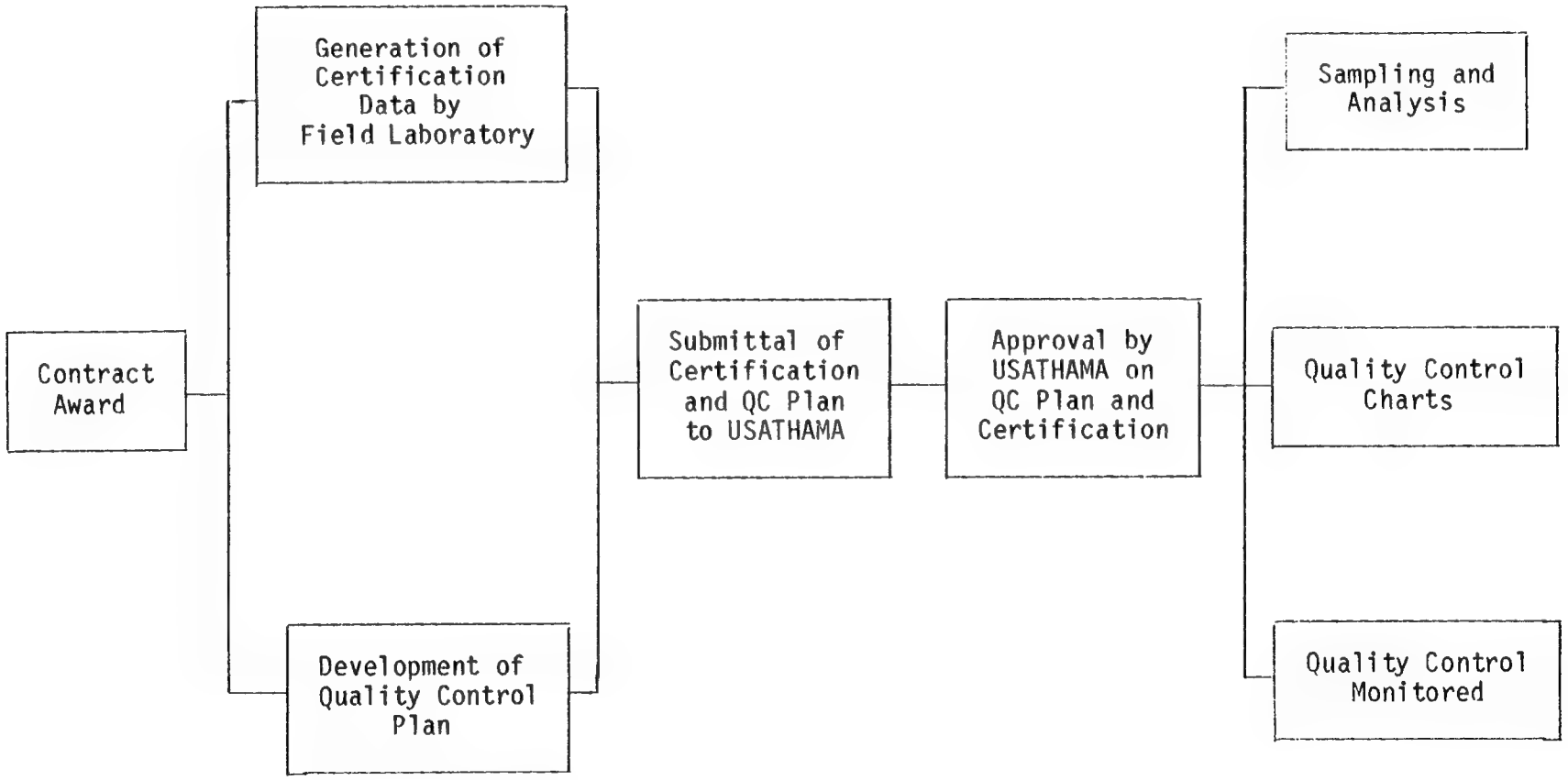
V. LABORATORY CERTIFICATION

A. INTRODUCTION:

Prior to using an analytical method for the analyses of natural samples, the Field Laboratory must be certified for that method. The Field Laboratory must submit to USATHAMA a written method report, with accompanying data, according to the format prescribed in Appendix 1.

The Field Laboratory must submit a Quality Control Plan specific to the USATHAMA program(s) being supported.

SEQUENCE OF EVENTS



B. LABORATORY CERTIFICATION:

1. Laboratories.

a. The confidence in any analytical method is limited if the analyst has not demonstrated skill in performing the analysis. Therefore, the analyst will be:

- Trained in quality control techniques.

- Required to qualify to run the analysis.

b. The qualification test results must be statistically valid and must include evaluation of precision and accuracy.

c. When more than one person has qualified to do the same test, replicate data will be compiled to validate not only the method but the performer.

d. It is advantageous that new labs submit a single method for compliance before all methods are submitted.

e. Laboratories will demonstrate their proficiency in conducting chemical analyses by analyzing spiked standard samples using the analytical method intended for use in the program being supported. Analysts will demonstrate proficiency for each analytical method that they will perform prior to conducting analyses of natural samples.

B. LABORATORY CERTIFICATION (Cont)

2. Standard Samples for Certification.

a. Standard samples will be prepared as outlined in Section VII.E.3 (Standard Samples).

b. Standard samples will be spiked with the analyte(s) of interest at:

- Blank
- 0.5 times the desired/required detection limit (DL)
- 1.0 times the desired/required detection limit (DL)
- 2.0 times the desired/required detection limit (DL)
- 5.0 times the desired/required detection limit (DL)
- 10.0 times the desired/required detection limit (DL)

3. Certification for Semi-Quantitative Analysis.

a. A minimum of one sample at each concentration level (0 (blank), 0.5 DL, 1DL, 2DL, 5DL, 10DL) will be analyzed in a single day.

B. LABORATORY CERTIFICATION (Cont)

b. The detection limit will be calculated using the equations outlined in Section X.

c. The precision for semi-quantitative analyses will be reported as "999." on data management entries.

d. The accuracy will be the slope of the best fit linear regression line of found versus target concentrations.

e. The best fit linear regression line must have a correlation coefficient of 0.996 for the calculation of the detection limit and accuracy. Exceptions to this criterion must be approved by the USATHAMA Analytical Branch.

4. Certification for Quantitative Analysis.

a. A minimum of one sample at each concentration level (0 (blank), 0.5DL, 1DL, 2DL, 5DL, 10DL) will be analyzed each day for four separate days. The four days should be consecutive if at all possible.

b. The detection limit will be calculated using the equations outlined in Section X as applied to the data generated over the four days of certification.

B. LABORATORY CERTIFICATION (Cont)

c. The precision of the method will be the standard error of the best fit linear regression line of found versus target concentration values for the data generated over the four days of certification testing.

d. The accuracy of the method will be the slope of the best fit linear regression line of found versus target concentration.

5. Certification for Qualitative Analysis.

a. A minimum of three standard samples spiked at the desired/required detection limit and three standard sample blanks will be analyzed in a single day using the complete analytical method.

b. The results of these analyses will be subjected to the rank sum test to determine if the spiked samples can be differentiated from the blank samples.

(1) If the analyses result in numerical values:

(a) Arrange the values in ascending order.

(b) Assign ranks to each value in order, i.e., assign 1 to the smallest, 2 to the second smallest, and so on. In the event

of ties for ranks, the mean of the ranks that are tied is assigned to each of the values.

(c) Sum the ranks from the blanks. This sum will not exceed six for acceptable certification.

(2) If the analyses result in qualitative descriptions, i.e., positive or negative:

(a) Arrange the results according to the qualitative responses.

(b) Assign ranks to the responses. In the case of groupings such as positive and negative, the mean of the ranks for each group will be assigned to each response in the group.

(c) Sum the ranks from the blanks. This sum will not exceed six for acceptable certification.

c. If the analytical results from the six samples (three spikes and three blanks) fail the certification test, an additional blank and spike may be analyzed.

B. LABORATORY CERTIFICATION (Cont)

(1) The analytical results from the additional blank and spike will be combined with the results from the original six samples.

(2) The resultant eight responses will be subjected to the rank sum test as outlined above.

(3) For acceptable certification, the sum of the ranks from the blank samples must not exceed 12.

d. If the testing fails certification, the method is considered incapable of distinguishing between blanks and the spiked concentration level. The required/desired detection limit concentration must then be increased to a level at which the method is capable of distinguishing the spikes from the blanks. If the required/desired detection limit cannot be altered, another analytical method must be selected to obtain the desired sensitivity.

e. No estimates of precision and accuracy will be reported for qualitative analyses.

B. LABORATORY CERTIFICATION (Cont)

6. Data Acceptance.

a. Certification testing data need not have been generated during the performance period of the USATHAMA tasking (under contract to USATHAMA). Data generated by the Field Laboratory prior to involvement in USATHAMA programs is acceptable provided the data are the same as required in Section V.B.3, 4, or 5.

b. Once a laboratory is certified to perform an analytical method for one USATHAMA program, the certification will normally suffice for other USATHAMA programs and need not be repeated unless certification requirements have changed.

7. Documentation.

a. Documentation on the analytical certification testing will be submitted to the USATHAMA Analytical Branch for review. This documentation will be in the format as outlined in Appendix 1. Analytical methods will be reviewed and approved by the USATHAMA Analytical Branch prior to use in USATHAMA programs. Methods will be submitted in the format in Appendix 1 to describe the exact procedures and materials required to analyze samples. Data to support the limitations (precision, accuracy, and detection limits) of the method will be submitted concurrently to demonstrate the applicability to the desired analyses. Procedures for methods given

B. LABORATORY CERTIFICATION (Cont)

to Field Laboratories by USATHAMA as approved methods need not be resubmitted for approval unless modifications have been made. However, data specific to the certifying laboratory (e.g., tested range, sensitivity, detection limit, etc.) must be submitted. Modifications to approved methods will be submitted to the USATHAMA Analytical Branch for approval before use. Any change in the documented procedure will constitute a modification; the Analytical Branch will determine the significance of the modification. Significant modifications will require the generation of additional precision, accuracy, and detection limit data to either demonstrate that the previous estimates of the limitations are still valid or develop the necessary data to accurately describe the new method.

b. Upon completion of the certification testing, performers will provide a narrative evaluation, apart from the Appendix 1 format, of each analytical method. This evaluation will include:

(1) A statement as to the effectiveness of the analytical method for its intended use to include the significance of the precision, accuracy, and detection limit in achieving the objectives of the program being supported.

(2) A statement on shortfalls of the analytical method.

B. LABORATORY CERTIFICATION (Cont)

8. Approval.

a. If the documentation indicates that the laboratory is proficient in conducting the given analysis, the Analytical Branch will approve the laboratory for performing routine analyses using that particular method.

b. Upon approval from the Analytical Branch, the Data Management personnel will be notified to accept data from that method for storage in the Data Management System.

9. Methods Not Requiring Certification.

a. Some analytical methods are considered not amenable to certification. Laboratories requested to perform such analyses in support of USATHAMA programs are still required to document the procedures for these analyses although not necessarily in the format in Appendix 1. Sufficient information must be documented in test plans, technical plans, QC plans, etc., to describe exactly what procedures were used to perform these analyses.

b. Methods not requiring certification must be declared as such by the USATHAMA Analytical Branch. Some of the methods currently considered as not certifiable are:

B. LABORATORY CERTIFICATION (Cont)

(1) pH.

(2) Biochemical oxygen demand (BOD).

(3) Chemical oxygen demand (COD).

(4) Oil and grease.

(5) Total organic carbon (TOC).

(6) Hardness.

c. Other methods that may be included in this category should be brought to the attention of the USATHAMA Analytical Branch for consideration.

C. FIELD LABORATORY QUALITY CONTROL PLAN:

1. Introduction.

Prior to initiating analyses of field samples in support of USATHAMA programs, Field Laboratories will develop a detailed quality control (QC) plan specific to the project being supported. The QC plan will be submitted to the USATHAMA Analytical Branch for approval.

2. Purpose.

The purpose of the Field Laboratory Quality Control Plan is to (a) establish procedures to ensure that analytical systems are under control; and (b) recognize and correct out-of-control situations.

The USATHAMA Analytical Branch recognizes the fact that the implementation of these procedures is dependent upon operations in the Field Laboratory. These operations may differ markedly from laboratory to laboratory. For these reasons, the Field Laboratory QC Plan must address those situations, particular to its laboratory, that are not covered by the USATHAMA QA Program. An example Table of Contents for a QC Plan is shown in Appendix 2. Field Laboratory QC Plans should not be restricted to only those subjects noted.

C. FIELD LABORATORY QUALITY CONTROL PLAN (Cont)

3. Content of Quality Control Plans.

Quality Control Plans will include, as a minimum, the following information and descriptions:

a. A statement or reference of adherence to the USATHAMA QA Program.

b. A detailed account of how the Field Laboratory will implement the USATHAMA QA Program.

c. Organization and responsibilities of the Field Laboratory.

d. Sampling, preservation, and shipment of samples.

e. Inspection and logging in.

f. QC sample introduction and lot sizing.

g. Instrument calibration.

h. Logs (instrument, sample, QC).

i. Reference materials.

j. Control charts.

C. FIELD LABORATORY QUALITY CONTROL PLAN (Cont)

k. The methods and criteria for determining when an analytical system is out of control.

l. What actions will be taken to correct an out-of-control situation and how the actions will be reported and documented.

m. List of personnel responsible for data review and sequence of review prior to submittal.

D. VISITS TO FIELD LABORATORIES:

Representatives of the USATHAMA Analytical Branch and/or the Central QA Laboratory will visit the Field Laboratories to discuss aspects of quality assurance/quality control.

After reviewing the Field Laboratory's proposed QC Plan, the Field Laboratory will be visited to discuss any weaknesses in the plan, to evaluate the laboratory's capability to implement the plan, and to discuss any discrepancies in the certification documents, etc. During this visit, the USATHAMA representative will fill out the Checklist for Laboratory Adherence (Appendix 3). Copies of the completed checklist will be provided to the Field Laboratory Chief and the USATHAMA Analytical Branch. This visit will occur before analyses of field samples are initiated by the Field Laboratory.

After initiation of the analyses by the Field Laboratory, a USATHAMA representative will visit the Field Laboratory to evaluate the effective implementation of the local QC Plan. Quality control practices, such as maintenance of control charts, will be evaluated during this visit. Findings will be reported to the Field Laboratory Chief and the USATHAMA Analytical Branch.

Scheduling/completion of the visits noted above does not preclude any additional visits.

VI. LABORATORY CONTROL PROCEDURES FOR USE DURING ROUTINE ANALYSIS

VI. LABORATORY CONTROL PROCEDURES FOR USE DURING ROUTINE ANALYSIS

A. INTRODUCTION:

The purpose of this section is to ensure Quality Assurance in sampling and analysis by the use of Control Samples, Control Charts, Reference Materials, and Instrument Calibration. To successfully comply with the USATHAMA Quality Assurance Program, it is essential that controls are initiated and maintained throughout the analysis of samples.

Specifically, each testing lot must contain at least one control sample. It is imperative that the type of control sample selected - blank, duplicate, spike, etc. - provide the desired effect (Section B cites the correct usage for each type of control sample). Data generated from the control samples are then plotted on control charts used to monitor the day-to-day variations in the precision or accuracy of routine analyses.

Upon completion of the analytical effort, the FQAC (in coordination with the Field Laboratory Director) will provide, to the USATHAMA Project Officer, the control sample data as well as specific observations delineating the effectiveness of the control samples for each analytical method.

1. These observations will include rationale for each of the following:

   a. Selection of the samples used for blanks, the samples used for spikes, and the samples used for duplicates, etc.

A. INTRODUCTION (Cont)

b. Spike levels.

c. Number of blanks, spikes, and duplicates.

2. If, at any time during the analytical effort, a process was not in control, a discussion will be submitted on:

a. What actions were taken to bring the process back into control.

b. What actions were taken to ensure that the out-of-control situation did not occur.

c. What was done with all of the data which were obtained while the process was out-of-control.

B. CONTROL SAMPLES:

Control samples are those samples that are introduced into the train of actual samples as a monitor on the performance of the analytical system. A control sample may consist of a standard or natural matrix.

Types of Control Samples.

1. Duplicates can provide indications of the precision of the analytical system. They will not provide indications of matrix effects or accuracy.

2. Method blanks can provide an indication of positive interferences introduced within the laboratory. They will not provide information on matrix effects, accuracy, precision or natural background. Matrices to be used for control blanks must be determined to be free of contamination prior to use.

3. Spikes in standard matrices can provide information on accuracy but will not indicate matrix effects or natural background levels.

4. Spikes of natural samples in conjunction with analyses of unspiked natural samples can provide information on matrix effects, natural background, and accuracy.

B. CONTROL SAMPLES:

5. Field blanks can provide an indication of positive interferences introduced in the field and in the laboratory. They will not provide information on matrix effects, accuracy, precision, or natural background. Matrices to be used for control blanks must be determined to be free of contamination prior to use.

C. CONTROL CHARTS:

1. Introduction.

Control Charts are used to monitor the variations in the precision or accuracy of routine analyses and can detect trends in these variations. The construction of a control chart requires initial data to establish the mean and standard deviation of measurements. Measurements to be used in the data base are obtained from performing the complete analytical method.

In the initial construction of the control charts, data from the laboratory certification analyses will be used. Spiked control samples in standard matrices will be inserted in each lot of samples to demonstrate that analyses of that lot are under control.

Precision and Accuracy Control Charts will be used in this QA Program.

2. Precision Control Charts.

a. Precision control charts are constructed by calculating the mean and standard deviation of the found concentrations at a single target concentration.

b. The mean found concentration will be the central line of the control chart.

C. CONTROL CHARTS (cont)

c. Control limits will be established based on the standard deviations.

- The upper warning limit (UWL) and lower warning limit (LWL) will be established at twice the standard deviation (2S) above and below the central line and will be expressed as a found concentration.

- The upper control limit (UCL) and lower control limit (LCL) will be established at three times the standard deviation (3S) above and below the central line and will be expressed as a found concentration.

d. Found concentrations of QC spiked standard matrix samples from day-to-day analyses will be plotted on the control charts for the particular target concentrations.

- The majority of values should fall within the bounds of the UWL and LWL. The process is then considered in control.

- Some data may fall between the UWL and UCL or the LWL and LCL. An occasional point in this area may be expected but two such values in a single day or in consecutive days indicates an out-of-control situation. Such a situation requires corrective action.

C. CONTROL CHARTS (cont)

- Data falling outside the UCL and LCL will be considered indicating an out-of-control situation.

- In all situations, corrective actions will be taken to ascertain the cause of the out-of-control situation.

e. After the day's data have been plotted on the control chart, the data will be pooled with previous data to calculate a new mean and standard deviation. These will be used for controlling the following day's process. In determining the new mean and standard deviation, the new data should be combined with the individual values of previous found concentrations and not the mean of the previous found concentrations.

f. No data may be discarded unless sufficient reason can be cited to justify the discarding process. That a point is beyond control limits is not, in itself, sufficient justification to discard the point.

g. Since precision control charts must be constructed at specific target concentrations, day-to-day QC samples must be spiked at these concentrations. Concentrations of QC samples must be carefully chosen to cover the range of the method.

C. CONTROL CHARTS (cont)

3. Accuracy Control Charts.

a. Accuracy control charts are constructed by calculating the mean and standard deviation of the slope of the least squares regression line of a plot of found versus target concentrations.

b. The mean slope will be the central line of the control chart.

- The slope, b, of the regression line from data obtained on a single day will be calculated according to the formula:

$$b = \frac{\Sigma XiYi - \Sigma Xi\Sigma Yi/N}{\Sigma Xi^2 - (\Sigma Xi)^2/N}$$

where Yi = the ith found concentration

Xi = the ith target concentration

N = number of XY pairs

and Σ indicates the sum from i = 1 to i = N.

- A slope is calculated for each day of analysis from the data obtained on that day. A minimum of three data points (XY pairs) is necessary to determine a regression line and, consequently, the slope of the line.

C. CONTROL CHARTS (cont)

- The slopes from several days are averaged to obtain the mean slope over all days.

c. Control limits will be established based on the standard deviation, s, of the slopes of the lines when the slopes from several days are averaged.

- The upper warning limit (UWL) and lower warning limit (LWL) will be established at twice the standard deviation (2S) above and below the central line and will be expressed as the slope.

- The upper control limit (UCL) and lower control limit (LCL) will be established at three times the standard deviation (3S) above and below the central line and will be expressed as the slope.

d. The slope of a line calculated from the found concentrations of QC spiked standard matrix samples analyzed in a single day will reflect the accuracy for that day. The correlation coefficient for each daily regression line will be greater than or equal to the correlation coefficient obtained during certification.

- The value of the slope will be plotted on the control chart.

- The majority of the values should fall within the bounds of the UWL and LWL. The process is then considered in control.

C. CONTROL CHARTS (cont)

- Some data may fall between the UWL and UCL or the LWL and LCL. An occasional point in this area may be expected, but consistent values in this range indicate an out-of-control situation and require corrective action.

- Data falling outside the UCL or LCL will be considered indicative of an out-of-control situation.

- Corrective actions will be taken to ascertain the cause of all out-of-control situations.

e. After the slope from the day's data has been determined, this value will be pooled with the slopes obtained from previous days to calculate a new mean and standard deviation to control the following day's process. Except for the data obtained from standard samples, no data may be discarded unless sufficient reason can be cited to justify the discarding process. That a point is beyond control limits is not sufficient justification to discard the point.

f. The required minimum three points to define the slope of the line will be positioned approximately at the midpoint and at the upper and lower extremes of the range of the method.

C. CONTROL CHARTS (cont)

4. Out-of-Control Situations.

a. An out-of-control situation may be indicated by:

- A value outside the control limits.
- A series of seven successive points on the same side of the central line.
- A series of five successive points going in one direction.
- A cyclical representation of control values.

b. When an out-of-control situation is detected, efforts will be initiated to determine the cause. Corrective actions will be taken to bring the process under control.

c. The out-of-control situation and corrective actions taken must be fully documented.

d. Data obtained since the last in-control QC sample will be considered invalid and will not be used in subsequent data analyses to support conclusions or recommendations. Analyses will not be continued until the process is determined to be under control.

C. CONTROL CHARTS (cont)

e. In order to demonstrate that the process is again in control, the following conditions must be met:

- Precision:

  A minimum of two successive control samples must lie within the control bounds.

- Accuracy:

  A minimum of three control samples at different concentrations (DL, 5DL, and 10DL) will be analyzed, and the resultant slope of the regression line must fall within the three standard deviation control limits. The correlation coefficient must be greater than or equal to the correlation coefficient obtained during certification.

VII. SAMPLE MANAGEMENT, COLLECTION AND PREPARATION

VII. SAMPLE MANAGEMENT, COLLECTION, AND PREPARATION

A. INTRODUCTION:

The objective of the procedures in this section is to obtain samples which represent the matrix being tested. Trace levels of contaminants from external sources must be eliminated through the use of good sampling techniques.

Sample management and stringent documentation are the key to successful quality assurance.

It should be noted that sampling and sample preparation of biological tissues are not covered by this plan. When biological sampling requirements are identified, detailed protocols will be established in coordination with the USATHAMA Analytical Branch and Army biological expertise on a case-by-case basis.

B. SAMPLE MANAGEMENT:

The management of samples, up through the point of designating the aliquot to the analyzed, will be under the supervision of the FQAC.

- The FQAC will make unannounced trips to the site to inspect the sampling. Each major type of sampling, e.g., groundwater, surface water, soil, sediments and biota (if applicable), will be inspected at least once during these trips. The FQAC will document each inspection and ensure that procedures described in the scope of work are followed.

- The FQAC will ensure that samples are being labeled, preserved, stored, and transported according to the prescribed methods.

- If the FQAC determines that significant deviations from the sampling protocol have occurred, resulting in a compromise of the sample integrity, all samples taken prior to the inspection, subsequent to any previous inspection, will be discarded and fresh samples taken.

- The FQAC will introduce control samples (duplicates, spikes, and blanks) into the sample flow in an inconspicuous fashion. A random introduction of control samples should be accomplished during the logging in process without leaving such clues as a sudden perturbation in the sequence of laboratory numbers or the appearance of a cleaned up extract in a group of soil samples.

B. SAMPLE MANAGEMENT (Cont)

- The FQAC will assign internal laboratory identification numbers to all incoming samples and quality control (QC) samples according to the format in Section IX.B of this document. The identification numbers will be sequential and will be maintained in a bound log book to associate the number with the sample. During the assignment of the internal identification numbers, the FQAC will establish the sample lots and sample order within each lot ensuring that QC samples are included within each lot. Identification numbers within a lot will be sequential.

C. SAMPLE COLLECTION

1. Volatiles.

a. Water.

- When sampling water for volatile compounds, care must be exercised to prevent loss of the compound through evaporation. Precautionary measures to be taken include:

  (1) Preclude aeration of the sample with any gas.

  (2) Fill bottles to capacity with samples.

  (3) Analyze as soon as possible after sampling.

b. Air.

- Air sampling for volatile compounds depends on sampling time, flow rate, and the collection device. Since the determination of the concentration of a contaminant in air is so highly dependent on the collection parameters and efficiencies, the collection procedure is considered an integral part of the analytical method for air samples and will be included in the method documentation.

C. SAMPLE COLLECTION (Cont)

c. Soils and Sediments

- Analyses for volatiles in soils and sediments are not normally performed in USATHAMA programs since the required sample handling (drying and homogenation) presents an opportunity for loss of analyte.

C. SAMPLING (cont)

2. Groundwater.

All groundwater sampling will be done after the wells have been properly developed. Because drilling and well construction disturb the natural groundwater system, some time should pass before sampling to allow the groundwater system to return to chemical equilibrium.

a. Procedures for Sampling Monitor Wells.

(1) Measure the depth from the top of the well casing (not protective casing) to the top of the water. Record the depth for future use in the development of the groundwater contour map. All measuring devices used in the well must be thoroughly rinsed with distilled water prior to use.

(2) Measure the depth from the top of the casing to the bottom of the sediment/water interface for initial sampling of a new well.

(3) Subtract the depth to top of the water from the depth to the bottom of the casing to determine the height of standing water in the casing.

(4) Remove a quantity of water from the well equal to five times the calculated volume of water in the well.

C. SAMPLE COLLECTION (Cont)

(5) If the well goes dry during pumping or bailing, allow the well to recover and again empty the well.

(6) Obtain a sample for chemical analyses immediately after pumping or bailing is complete. In case a well is pumped or bailed dry, and recovery is very slow, obtain a groundwater sample as soon as possible after the well has recovered.

(7) The sampling bailer or pump must be flushed with distilled water after sampling to prevent cross contamination between sampling wells. Materials incidental to sampling such as bailer ropes and tubing must also be flushed with distilled water. Sampling equipment must be protected from ground surface contamination by clean plastic sheeting. No sampling should be accomplished when wind blown particles may contaminate the sample or sampling equipment.

(8) All samples for organic chemical analyses should be placed in amber glass bottles with teflon lined lids. Samples for inorganic chemical analyses should be placed in polyethylene bottles. The sample bottle should be partially filled with the water to be sampled, and the contents should be agitated and discarded. The cap should be rinsed with the water to be sampled. The bottle should be filled to the top and capped securely. The sample bottle should be placed in a temperature

controlled (4°C) chest immediately after sampling and delivered to the laboratory as soon as possible.

(9) When the sample is taken, follow procedures outlined in Section VII.D, Sample Preservation.

b. Procedures for Sampling Water Supply Wells.

(1) From existing well data or an estimate of well depth, calculate the maximum possible volume of water in the well casing.

(2) Pump to discard at least five times the estimated volume of water in the well.

(3) Prior to taking samples, ensure that the water to be sampled is raw (untreated) water. Under no circumstances should treated water be taken for chemical analysis to define the levels of contamination in the aquifer.

(4) If holding or pressure tanks are used in the water supply system, they should be bypassed to obtain good representative ground-water samples.

(5) All samples for organic chemical analyses should be placed in amber glass bottles with teflon lined lids. Samples for

inorganic chemical analyses should be placed in polyethylene bottles. The sample bottle should be partially filled with the water to be sampled, and the contents should be agitated and discarded. The cap should be rinsed with the water to be sampled. The bottle should be filled to the top and capped securely. The sample bottle should be placed in a temperature controlled (4°C) chest immediately after sampling and delivered to the laboratory as soon as possible.

(6) When the sample is taken, follow procedures outlined in Section VII.D, Sample Preservation.

C. SAMPLE COLLECTION (Cont)

3. Surface Water.

Surface water samples may be obtained under varying circumstances. The sampling procedures in EPA 600/4-77/039, "Sampling of Water and Wastewater" must be considered in obtaining surface water samples.

4. Air.

a. Air sampling normally involves a pump to force air through a collection device. Since air passing through a pump may become contaminated, the pump should be placed in the sampling train so that the air passes through the collection device before passing through the pump.

b. Determination of the concentration of an analyte in air is dependent on the rate and time of sampling. The rate of sampling is dependent on the capacity of the pump and the restrictions in the sampling train. Sampling rates should be measured in the complete sampling train, and the measurement process should not alter the flow through the primary sampling route. Additionally, the point of measurement in the train should be at the air inlet to the collection device to preclude contributions to the measured flow from leaks.

c. Sampling time is of critical importance since, at a given flow rate, the volume of air sampled is time dependent. Initiation and

completion of sampling time should be accurately recorded to allow calculation of the total volume sampled.

d. The efficiency of the collection device should be determined during the development of the analytical method. Collection efficiency may be dependent on the sampling rate and time. Consequently, when using an analytical method, neither the sampling time nor rate should exceed the time or rate for which reliable data exist.

5. Soils.

a. Prior to sampling, surface vegetation, rocks, leaves and debris will be cleared from the sample point to allow collection of a clean soil sample.

b. Efforts will be made to ensure that samples are representative of the areas being investigated. A large area will require the collecting and compositing of multiple samples into a single sample to represent the area. This does not preclude the collection and analysis of the individual samples to describe the sampling points within the area.

C. SAMPLE COLLECTION (Cont)

c. Soil samples will be stored and shipped in wide-mouth amber glass bottles which have been thoroughly cleaned according to procedures outlined in Appendix 4.

d. Sample containers will be marked to indicate sampling date, time and location.

6. Sediments.

a. Prior to sampling sediments in a stream, the sampling device will be rinsed with stream water a point downstream from the sampling location to avoid disturbing the sediments at the sampling point. Also, sampling will be accomplished upstream of any disturbances in the stream caused by the sampler or sampling team.

b. Prior to sampling sediments in a pond or lagoon, the sampling device will be rinsed with water near the sampling point. However, caution must be exercised to avoid disturbing the sediments at the sampling point by the rinsing activities.

c. The type of samples to be used will be dictated by the nature, as well as the accessibility, of the sediments. In addition, the type of sampler chosen should be appropriate for obtaining the desired sample, i.e., a core sampler should not be used to obtain top sediment.

C. SAMPLE COLLECTION (Cont)

d. Sediment samples will be stored and shipped in wide-mouth amber glass bottles which have been thoroughly cleaned according to the procedures outlined in Appendix 4.

e. Sampling devices will be carefully rinsed with water from the sampled stream, pond or lagoon prior to sampling and with water from a USATHAMA designated source after each set of samples is collected at a particular sampling area.

f. Sample containers will be marked to indicate sampling date, time, location and depth.

D. SAMPLE PRESERVATION:

Procedures.

1. To prevent or retard the degradation/modification of chemicals in samples during transit and storage, the samples will be preserved and stored as outlined in Appendix 4 for the compounds of interest.

2. Efforts to preserve the integrity of the samples will be initiated at the time of sampling and will continue until analyses are performed.

3. Those samples containing organic compounds will be preserved immediately by refrigeration at or below 4°C and stored in amber glass bottles with teflon-lined lids. These bottles and lids will be cleaned as outlined in Appendix 4.

4. Those samples containing inorganic compounds will be stored in plastic polyethylene containers.

E. SAMPLE PREPARATION:

1. Water Samples.

a. Prior to analysis, well water samples will be filtered through a 0.45 micron filter to remove suspended particulate matter. Samples for analyses of volatile compounds will not be filtered. Samples for metals analyses must be filtered in the field prior to preservation. Any exceptions to this procedure must be approved by the USATHAMA Analytical Branch. The filter material must be suitable for the intended analysis. Materials known to adversely affect the analytical procedure must not be used.

b. Water used in the course of organic analyses (dilutions, standard samples, etc.) shall conform to ASTM Type II grade.

c. Water used in the course of inorganic analyses shall conform to ASTM Types I, III, or IV.

2. Soil/Sediment Samples.

a. Solid samples are complex mixtures of components of varying particle size. Each particle may contain the constituents of interest at concentrations different than that contained on other particles. Large sampling errors can result from selecting soil samples which contain a limited number of particles. Since the magnitude of the

E. SAMPLE PREPARATION (Cont)

sampling error is a function of: (1) particle size; (2) heterogeneity of the material sampled; and (3) the relative density of the compounds present; the minimum sample size must be calculated according to the Methods of Harris and Kratochvil[2]. One should include in excess of 10^6 particles.

b. Particles which do not pass a US Series 600 micrometers sieve are discarded with other debris which would contribute an insignificant percentage of the total sample surface area.

c. Soils and sediments are not usually analyzed for volatiles since quantities of these compounds are ordinarily lost during the drying process. However, if these types of analyses are necessary to satisfy regulatory requirements, samples must be analyzed in their as-received condition.

d. A moisture determination in accordance with ASTM D2216-71, "Laboratory Determination of Moisture Content of Soil", will be made on an aliquot of each solid sample, after air drying, so that analytical data can be reported on a moisture-free basis.

e. Soil samples sent to the analytical laboratory will not be analyzed in their as-received condition (except as noted in c, above). Before any portion of a sample is taken for analysis, it will be spread out on the dull side of aluminum foil for air drying.

E. SAMPLE PREPARATION (Cont)

f. Extraneous material such as metal, wood, or stones, will then be removed by sieving the sample through a US Series 600 micrometers (old designation #30) sieve.

g. The analyst will obtain the portion necessary for his analysis by subsampling the sample to size. All subsampling must be accomplished with the aid of a riffle or by proper quartering techniques according to ASTM D346. If any portion of the sample is separated by a non-approved method, the integrities of the portion taken and the remainder of the sample are considered to be compromised, and the sample is considered non-representative.

3. Standard Samples.

a. Water Samples.

(1) Organic Analysis

Standard samples for organic analyses will be prepared by adding the analyte of interest to distilled water (ASTM Type II) containing 100 mg/l each of both sulfate and chloride. The standard water is made by the following method:

(a) Weigh - 1.48 g of reagent grade anhydrous sodium sulfate into a 1 liter volumetric flask, dilute to mark.

E. SAMPLE PREPARATION (Cont)

(b) Weigh - 1.65 g of reagent grade dry sodium chloride into a 1 liter volumetric flask and dilute to mark.

(c) Transfer 100 ml of each of the solutions prepared above into a 1 liter flask and dilute to mark with water. This solution should be 100 mg/l in sulfate and chloride.

(2) Inorganic Analysis

Standard samples for inorganic analyses will be prepared by adding the analyte(s) to deionized water.

b. Soil/Sediment Samples.

(1) Standard samples for soil analyses will be prepared by adding the analyte to a sample of standard soil.

(2) To obtain a standard soil, soil will be obtained from the area (installation) of interest. Locations must be carefully chosen so that background samples, rather than contaminated samples, are collected.

(3) High background levels of contaminants, particularly inorganic cations and anions, sometimes cannot be avoided. When the background levels exceed the required/desired detection limits of

the analytes, the USATHAMA project officer will be informed, and he will decide if another soil sample is needed or if the required/desired detection limits must be raised.

(4) The soil will be air-dried and passed through a US Series 600 micrometers sieve. The soil is then mixed thoroughly by riffling or quartering.

(5) Sufficient soil must be collected initially so that the quantity available is adequate to support the entire program without having to obtain a second lot of soil.

4. Spiked Samples.

a. Water Samples.

(1) Water samples will be spiked by the addition of a known quantity of analyte to a known quantity of water sample. Spiking may involve addition of pure analyte or a solution of the analyte.

(2) When solutions are used for the spiking process, the solvent must be miscible with the water sample being spiked. When organic solvents are used as the spiking solution solvent, the volume of the spiking solution used should be kept to a minimum to prevent undue alteration of the aqueous character of the final solution.

(3) When spiking natural water samples, the concentration of the analyte initially present in the sample must be known. The amount of analyte added in the spiking process must be judiciously chosen so that the increment can be distinguished from the existing level. On the other hand, the amount of analyte added should not be so large that the final concentration of the sample is outside of the concentration range of concern or beyond the range of the analytical method.

b. Soil/Sediment Samples.

(1) Soil and sediment samples will be spiked by the addition of a known quantity of analyte to a known quantity of sample. Spiking is accomplished by completely wetting the sample with a solution of the analyte.

(2) The quantity of analyte to be added is dissolved in a volume of solvent previously determined to be just sufficient to wet the entire sample. This solution is poured over the bulk of the sample, and the mixture is allowed to stand for at least one hour.

(3) The spiking solvent is allowed to evaporate. This step can be expedited if a relatively volatile solvent is chosen for the spiking solution.

E. SAMPLE PREPARATION (Cont)

(4) The soil sample is then thoroughly mixed by riffling or quartering.

(5) Many soil samples contain high concentrations of analytes, particularly inorganic cations and anions. The amount of analyte added in the spiking process must be judiciously chosen so that the increment can be distinguished from the existing level. On the other hand, the amount of analyte added should not be so large that the final concentration of the sample is outside of the concentration range of concern or beyond the range of the analytical method.

VIII. ANALYSIS OF SAMPLES

VIII. ANALYSIS OF SAMPLES

A. ANALYTICAL METHODS:

1. Introduction.

An analytical method is a series of procedures or steps that must be performed to estimate the quantity of analyte in a sample. Methods must be documented so that variations in the procedures that would constitute a different method will be easily recognized. The USATHAMA policy described in this QA Program is to document and approve each method (analytical system) before its use and to adequately control each system as it is used.

2. Acceptable Methods.

a. Published methods of analysis (ASTM, AOAC, EPA, etc.) are acceptable for use in USATHAMA programs provided:

(1) Data are on hand to demonstrate the precision and accuracy of the method. As a minimum, these data must be the same as those generated for laboratory certification (Section V).

(2) The method is used in a manner for which it was intended. For example, a method of analysis for trace organics in drinking water may not be suitable for the analysis of industrial waste.

A. ANALYTICAL METHODS (Cont)

b. USATHAMA has developed methods of analysis for some chemical compounds. These methods are available for distribution to laboratories conducting analyses for these compounds for USATHAMA.

c. In the event that analyses must be conducted for compounds for which no reliable methods exist, development of a method will be pursued as outlined in Section C, Development of Analytical Methods.

B. ANALYTICAL PROCEDURES

1. Instrument Calibration.

a. Before samples are analyzed on an instrument, sufficient calibration standards of each analyte will be analyzed to establish that the instrument is functioning properly with the desired sensitivity. Economy dictates that analytes be combined in the same calibration standard when possible.

b. Instrument calibration will be accomplished using calibration standards prepared by mixing the species to be analyzed into the solvent that is introduced into the instrument as dictated by the analytical method. The concentration of the calibration standards will be chosen so as to cover the working range of the instrument.

(1) Initial calibration for semi-quantitative and quantitative analyses.

(a) Initial calibration procedures will be used whenever the instrument (1) is started up; (2) is used to analyze different analytes than those for which the instrument was previously calibrated during the present run; or (3) fails the daily calibration sequence.

(b) Calibration standards will be prepared and analyzed in the concentration series 0 (blank), 0.5X, X, 2X, 5X, and 10X,

where X is the concentration in the solvent being analyzed corresponding to the required or desired detection limit in the original matrix. For example, if the desired detection limit in the original matrix is one part per billion and a thousandfold concentration is required before introduction into an instrument, X would be one part per million.

(c) Data from the calibration standards will be plotted with the instrument response indicated on the ordinate and the concentration indicated on the abscissa.

(d) Data generated from this calibration procedure will be used to define the linear response range of the detector and will be used to determine the concentration of analytes in the solution introduced into the instrument.

(e) These data cannot be used to determine the detection limit of an analytical method unless the documented method requires an aliquot of the original sample to be introduced directly into the instrument.

(2) Daily calibration for semi-quantitative and quantitative analyses.

B. ANALYTICAL PROCEDURES (Cont)

(a) A minimum of three instrument calibration standards will be run prior to analyses each day to establish that the sensitivity of the instrument has not altered over the working range from the previous calibrations.

(b) The concentrations will be distributed so that the working range is bounded and one is at the approximate mid-point of the range.

(c) Data generated in this manner will be compared against the cumulative data to date to establish that the instrument response is stable within two standard deviations of the mean of previous determinations.

(d) A similar set of calibration standards will be analyzed at the end of each day to establish that the instrument response has not changed during the course of analyses.

(e) Exceptions to this procedure due to excessive analysis times or other mitigative factors must be first approved by the USATHAMA Analytical Branch.

(f) Introduction of calibration standards by the instrument operator during analysis will provide an early warning of instrument variances.

B. ANALYTICAL PROCEDURES (Cont)

(g) If significant variances (greater than two standard deviations from the mean of previous determinations) are observed in the calibration responses, the system is considered to have failed calibration. All data generated since the last satisfactory calibration are considered questionable and must be repeated.

(h) After calibration failure, the procedures for initial calibration must be followed to demonstrate satisfactory performance.

(3) Initial calibration for qualitative analyses.

(a) Initial calibration procedures will be used whenever the instrument (1) is started up; (2) is used to analyze different analytes than those for which the instrument was previously calibrated during the present run period; or (3) fails the daily calibration sequence.

(b) Calibration standards will be prepared and analyzed in concentrations of 0 (blank), and X, where X is the concentration in the solvent being analyzed corresponding to the required/desired detection limit in the original matrix. For example, if the desired detection limit in the original matrix is one part per billion and a thousandfold concentration is required before introduction into an instrument, X would be one part per million.

B. ANALYTICAL PROCEDURES (Cont)

(c) At least three of each of the concentrations (blank and spike) will be analyzed.

(d) The results of these analyses will be subjected to a rank sum test to determine if the concentrations can be distinguished from each other with 90 percent confidence. In the case of positive versus negative results, all three of the blanks must yield negative responses and all three of the spiked samples must yield positive responses.

(4) Daily calibration for qualitative analyses.

(a) A minimum of one blank and one calibration standard at X concentration (as defined above) will be run prior to analyses each day.

(b) A minimum of one blank and one calibration standard at X concentration (as defined above) will be run after completion of analyses each day.

(c) If any of the calibration standards yield an inappropriate response (positive for blank or negative for the spiked standard), the instrument is considered to have failed calibration. The cause of the failure must be determined and remedied before analyses are allowed to continue.

(d) If the calibration failure occurs during or at the end of the analyses of actual samples, the analytical results obtained since the last satisfactory calibration are considered questionable and must be repeated.

(e) After calibration failure, the procedures for initial calibration must be followed to demonstrate satisfactory performance.

c. For a direct injection method (i.e., when the sample matrix is introduced directly into the analytical instrument), standard matrix samples will suffice as calibration standards.

2. Semi-Quantitative Analyses.

a. Semi-quantitative analyses are used in USATHAMA programs to screen samples for the presence of unknown, as well as known, contaminants.

b. Prior to conducting semi-quantitative analyses, the Field Laboratory will have, on hand, the documented procedures in the format outlined in Appendix 1. The documentation for these methods will have been reviewed and approved by USATHAMA before utilization in USATHAMA programs. The Field Laboratory will have been certified to use these methods in the semi-quantitative mode using surrogate compounds as well as some of the actual analytes.

B. ANALYTICAL PROCEDURES (Cont)

c. While knowledge of the precision over the responsive range is not required for semi-quantitative analysis, knowledge of the detection limit range is critical to ascertaining the sensitivity of the method. The detection limit may be modified as results of control samples become available during the course of day-to-day analyses.

d. Instruments will be calibrated with the actual analytes or surrogate standards on each day in which analyses are conducted to demonstrate that the instruments are not a source of unnecessary error and are sufficiently stable and sensitive to perform intended analyses without frequent adjustment. See Section VIII.B.1.

e. During the analyses of natural samples, control samples will be included in each lot. In all instances, the control sample must be processed through the complete analytical method.

(1) One method blank must be included in each lot to verify that the laboratory is not a source of contamination. The method blank will be prepared in the appropriate standard matrix. Soil and sediment samples must be carefully chosen for use as standard matrices to ensure that natural concentration levels of contaminants do not interfere with the determination of the precision, accuracy, or detection limit of the method.

B. ANALYTICAL PROCEDURES (Cont)

(2) For gas chromatography/mass spectrometry analyses, deuterated surrogate standards will be spiked into each sample in the original matrix. The deuterated standards will be chosen so that they will elute early, midway, and late in the chromatographic run. The concentration level of the spikes will be chosen so that, in each lot, each standard will have been spiked at 2X, 5X, and 10X, where X is the detection limit obtained during certification.

(3) For gas chromatography and high performance liquid chromatography analyses, analytes considered to have an extremely low probability of being present at the area of concern will be used as surrogate standards. These surrogate standards will be chosen by agreement between the FQAC, the USATHAMA project officer, and the USATHAMA Analytical Branch. At least three surrogate standards will be chosen for each analytical method so that they will elute early, midway, and late in the chromatographic run. The original matrix of each sample will be spiked with each of the surrogate standards. The concentration levels of the spikes will be chosen so that, in each lot, each surrogate standard will have been spiked at 2X, 5X, and 10X, where X is the detection limit obtained during certification. Data from these surrogate standards will be used to update precision and accuracy control charts.

B. ANALYTICAL PROCEDURES (Cont)

(4) For analyses other than GC/MS, GC, and HPLC, at least three spiked standard matrix samples will be included in each lot. The samples will be spiked with the analyte(s) of interest so that, in each lot, each analyte will have been spiked at 2X, 5X, and 10X, where X is the detection limit obtained during certification. Data from these standard matrix samples will be used to update precision and accuracy control charts.

f. Results of analyses of natural samples will be reported by identifying the compound (or species) with estimates of the concentrations to one significant figure.

(1) Results will be reported in terms of concentration in the original matrix and will be corrected for recoveries based on the results of the analyses of the control samples described in Section VIII.B.2.3 above.

(2) When specific compounds are to be reported on, lack of indications of the presence of these compounds will be reported as "less than" the detection limit if the detection limit has been determined previously by the procedures outlined in Section V.B.3.

(3) Estimates of concentrations of species which have not been subjected to the detection limit procedure outlined in Section

V.B.3 may be reported based on the response compared to the response of a surrogate standard. The estimate may be based on the response of an internal standard provided that:

(a) The response of the species does not correspond to a concentration that is less than the detection limit of the internal standard.

(b) The detection limit of the internal standard has been estimated from analyses of spikes of the internal standard into the solvent being analyzed by the instrument. As with the calibration standards (see Section VIII.B.1.b(1)(b)), the concentrations of these spikes will be 0 (blank), 0.5X, X, 2X, 5X, and 10X. The detection limit will be calculated from these data according to the guidelines in Section X.B.

(c) The estimated concentration contains only one significant figure.

(d) The estimated concentration is annotated as based on the internal standard.

(e) The estimated concentration is reported as the concentration in the original matrix assuming 100% recovery.

B. ANALYTICAL PROCEDURES (Cont)

(4) Internal standards must be spiked directly into the matrix analyzed by the instrument.

3. Quantitative Analyses.

a. Quantitative analytical methods are used in USATHAMA programs to estimate the level of contamination of specific analytes in various matrices.

b. Prior to conducting quantitative analyses, the Field Laboratory will have, on hand, the documented procedures in the format outlined in Appendix 1. The documentation for these methods will have been reviewed and approved by USATHAMA before utilization in USATHAMA programs.

c. Instruments will be calibrated with the actual analytes and surrogate standards on each day in which analyses are conducted to demonstrate that the instruments are not a source of unnecessary error and are sufficiently stable and sensitive to perform intended analyses without frequent adjustment. See Section VIII.B.1.

d. Quality control samples will be inserted at random in the sample lot by the FQAC or his representative (who also has no direct responsibility in the analyses of samples). In all instances, the control samples must be processed through the complete analytical method.

B. ANALYTICAL PROCEDURES (Cont)

(1) At least one method blank will be included in each lot of samples to verify that the laboratory is not a source of contamination. The method blank will be prepared in the appropriate standard matrix. Soil and sediment samples must be carefully chosen for use as standard matrices to ensure that natural concentration levels of contaminants do not interfere with the determination of the precision, accuracy, or detection limit of the method.

(2) Types and quantities of control samples for specific instrumental analyses will be the same as those described for semi-quantitative analyses. See Section VIII.B.2.e.

(3) At least one duplicate natural sample must be included in each lot.

(4) Data from these control samples will be used to update precision and accuracy control charts and, by addition to the existing data base, to refine the detection limit, precision, and accuracy of of the method.

e. Estimates of concentration levels in quality control and actual samples will be reported to USATHAMA according to the Data Management User's Guide.

B. ANALYTICAL PROCEDURES (Cont)

(1) Reported values will be corrected for recoveries over the total analytical method to offer the best estimate of the actual concentration in the original matrix.

(2) Values less than the detection limit obtained during certification will be reported as "less than" the detection limit unless sufficient data exist to justify a lower detection limit on the particular day the value was obtained.

(3) Conversely, detection limits higher than the certified detection limit (as in the case of a sample with high background levels) will be reported as "less than" the higher detection limit.

f. The slope of the best fit linear regression line of found versus target concentration values from QC data in spiked standard samples obtained on the date of analysis will be reported as the accuracy.

g. The standard error of the best fit linear regression line of found versus target concentration values for QC data in spiked standard samples obtained on the date of analysis will be reported as the precision of the measurements for that day.

B. ANALYTICAL PROCEDURES (Cont)

4. Qualitative Analyses.

a. Qualitative analytical methods are used in USATHAMA programs to screen for the presence or absence of contaminants.

b. Prior to conducting qualitative analyses, the Field Laboratory will have, on hand, the documented procedures in the format outlined in Appendix 1. The documentation for these methods will have been reviewed and approved by USATHAMA before utilization in USATHAMA programs.

c. Instruments will be calibrated with the actual analytes or surrogate standards on each day in which analyses are conducted to demonstrate that the instruments are not a source of unnecessary error and are sufficiently stable and sensitive to perform intended analyses without frequent adjustment. For methods that result in visual responses from the reaction of contaminants with test solutions or devices (e.g., sorbent tubes), the quality of the test solutions or devices will be checked on each day analyses are conducted to ensure that degradation has not occurred. For disposable devices designed for one-time use, checks on selected devices in a lot will be adequate and will be done on each day analyses are conducted.

B. ANALYTICAL PROCEDURES (Cont)

d. Daily quality control on qualitative methods will consist of a standard matrix spike and a standard matrix blank. The spike concentration will be that level which is desired to be distinguished as contaminated.

e. Results of qualitative analyses will be reported either as (1) "positive" or "negative"; or (2) "greater than" or "less than" the spike concentration. The spike concentration will be restricted to one significant figure.

f. Maintenance of control charts for qualitative analyses are not necessary.

C. DEVELOPMENT OF ANALYTICAL METHODS:

1. In the event that analyses must be conducted for compounds for which no reliable methods exist, development of a method will be pursued by having the Development Laboratory (laboratory designated and/or contracted to develop an analytical method) submit Documentation for Proposed Methods Development (Appendix 5) to the USATHAMA Analytical Branch for approval prior to initiation of development.

2. The Analytical Branch will evaluate the proposed approach for technical soundness and economy of effort. The Analytical Branch will then request the Development Laboratory to proceed with the method development as proposed or with recommended modifications.

3. The Development Laboratory will investigate the proposed procedures to be included in the method. Should any of the proposed procedures approved by the Analytical Branch be found to be inadequate for the method, alternative procedures will be investigated after approval by the Analytical Branch.

4. When the analytical procedures have been completed by the Development Laboratory, the procedures will be documented according to the format in Appendix 1.

5. The Development Laboratory will generate precision and accuracy data as outlined in Section X.C and X.D on the proposed method in standard samples (see Section VII.E.3).

C. DEVELOPMENT OF ANALYTICAL METHODS (Cont)

6. Utilizing the precision and accuracy data, the detection limit will be calculated (see Section X.B) as well as the sensitivity at the detection limit for inclusion in the documentation of the method.

7. Full documentation of the method as outlined in Appendix 1 will be submitted to the USATHAMA Analytical Branch. The Analytical Branch will review the documentation for completeness and comprehension. Based on this review, the Development Laboratory will make any necessary modifications prior to approval of the method by the USATHAMA Analytical Branch.

8. Upon final approval of the documented method, the Analytical Branch will assign a number to the method. The method will be entered into the Data Management Methods File by the Development Laboratory. In the event that the Development Laboratory does not have a computer terminal link to the Central Computer, the method will be entered by USATHAMA.

D. REFERENCE MATERIALS:

1. Standard Analytical Reference Materials (SARMs).

In order to evaluate the accuracy of a chemical analysis, it is necessary to have an approved point of reference. Chemical analyses conducted in support of USATHAMA's programs are based on Standard Analytical Reference Materials (SARMs) which are developed and distributed by the Central Quality Assurance Laboratory. These materials either will be National Bureau of Standards (NBS) Standard Reference Materials or will be traceable to one of these materials. Although NBS offers only a limited selection of standards, it is possible to trace any substance through a series of comparisons to some other standard reference material. The traceability may be as tenuous as an indium standard being used to calibrate the Differential Scanning Calorimeter (DSC) which, in turn, is used to measure the melting point of a compound.

The Analytical Branch must review the suitability of each material and all its supporting data prior to distribution as a SARM. Guidelines for development of Standard Analytical Reference Materials are given in Appendix 6. NBS Standard Reference Materials are accepted at face value for use as SARMs, if the standard is to be used for the purpose for which it was intended. For instance, SRM #1632a (trace elements in coal) would not be an acceptable standard on which to base a high purity arsenic analysis. Commercially available standards may be accepted as SARMs if sufficient supporting data can be obtained from the vendor. These

supporting data are scrutinized in the same manner as that presented by the Central Laboratory in support of the SARMs it develops.

Samples of SARMs are shipped to Field Laboratories upon request of the USATHAMA Project Officer. Field Laboratories will report results of analyses based on SARMs or interim reference materials supplied by the Central QA Laboratory.

The Central QA Laboratory retains the bulk of each SARM in a repository at 0°C. At regular intervals, surveillance samples are removed from the repository and re-analyzed by the original acceptance methods. When the standard has deteriorated to the 98 mole percent purity level, Field Laboratories are warned to suspend use of the standard until a new lot can be supplied.

Field Laboratories will store all reference materials at 4°C.

D. REFERENCE MATERIALS (Cont)

2. Interim Reference Materials.

When it is necessary to run analyses before a SARM is available, interim reference materials may be used. However, the following precautions will be taken:

a. The interim reference material will be stored at 4°C and a portion will be retained for a comparison with the approved SARM when available.

b. When interim reference materials are obtained by the Field Laboratory, the following data will be recorded by the Field Laboratory as a minimum description of the material:

(1) Infrared spectrum.

(2) MP, decomposition point, or b.p.

(3) NMR spectrum.

(4) Elemental analysis.

(5) GC or LC (by difference).

D. REFERENCE MATERIALS (Cont)

c. When interim reference materials are supplied by the Central QA Laboratory to Field Laboratories, the Central QA Laboratory will be responsible for obtaining the data noted in b above.

IX. DATA MANAGEMENT

IX. DATA MANAGEMENT

A. LOGGING OF SAMPLES:

1. The accountability of a sample begins when the sample is taken from its natural environment. A bound log book will be maintained to record the taking of each sample. Entries will be made in waterproof ink.

2. The log book will contain information to distinguish each sample from any other sample. This information will include:

   a. The USATHAMA project for which sampling is being conducted.

   b. The matrix being sampled (air, groundwater, soil, etc.).

   c. The sampling date and time.

   d. The specific sampling location in sufficient detail to allow resampling at the same location.

   e. The method of sampling to include preservation techniques.

   f. Significant observations made during the sampling process.

   g. Signature of the person performing the sampling.

A. LOGGING OF SAMPLES (Cont)

3. A separate log book will be maintained for each USATHAMA project. Samples for the specific project will be the only entries in the log book.

4. Each sample entered in the log book will be assigned a unique identification number. The numbers will be in sequential order and will be noted in the log book beside the corresponding sample entries.

5. Identification numbers will be marked on the sample containers in waterproof ink.

6. Records will be maintained to document the chain of custody of the samples from the time of sampling to the time of analysis.

7. On arrival at the laboratory, samples will be logged into a bound laboratory log book specific to the USATHAMA project being supported. The information in this log book will include:

   a. The USATHAMA project being supported.

   b. The date of arrival of samples at the laboratory.

   c. The identification numbers of the samples.

A. LOGGING OF SAMPLES (Cont)

d. Observations concerning the conditions under which the samples arrived, e.g., broken containers, leakage, lack of temperature control, etc.

B. SAMPLE IDENTIFICATION NUMBERS

1. Reporting of data to the USATHAMA data management system will require the assignment of an identification number to each aliquot of a sample (to include quality control samples) to be analyzed. The format consists of six (6) alphanumeric characters.

   a. The first three characters are letters that indicate the analytical lot.

      (1) A different lot number will be used for each analytical method to be employed. Consequently, when a method is used to determine multiple analytes, the identification number will be the same for each analyte of a particular aliquot.

      (2) A different lot number will be assigned for each lot analyzed by a particular analytical method.

      (3) Lots will be designated sequentially so that the first lot is AAA, the second lot is AAB, the twenty-seventh lot is ABA, etc.

   b. The last three characters are numbers that indicate the sample within the lot. These numbers will be in sequential order beginning with 001.

2. As an example, six samples are received from the field for mercury, TNT, DNT, and pH analyses. Not all of the samples need to be

B. SAMPLE IDENTIFICATION NUMBERS (Cont)

analyzed for all of the analytes. The mercury analysis is limited to three samples per lot, and the pH determinations are limited to ten samples per lot. TNT and DNT are analyzed simultaneously with the same analytical method, and a lot is limited to six samples. The identification numbers may be assigned as shown in the table.

	Mercury	TNT	DNT	pH
Sample 1	AAA001	AAB001	AAB001	AAC001
Sample 2	AAA002	AAB002	AAB002	AAC002
Sample 3	AAD001	AAB004	AAB004	
Sample 4	AAD002	AAB005	AAB005	
Sample 5		AAE001	AAE001	AAC004
Sample 6		AAE002	AAE002	AAC005
QC Sample	AAA003			
QC Sample		AAB003	AAB003	
QC Sample		AAB006	AAB006	
QC Sample				AAC003
QC Sample	AAD003			
QC Sample		AAE003	AAE003	

a. The mercury analyses are conducted in two lots: AAA and AAD. The third samples in each lot are QC samples.

B. SAMPLE IDENTIFICATION NUMBERS (Cont)

b. The pH determinations are done in one lot AAC, and the third sample is a QC sample.

c. The trinitrotoluene (TNT) and dinitrotoluene (DNT) analyses are obtained from the same analytical method. Consequently, the identification numbers in a single determination for TNT and DNT are identical. The analyses for these two compounds are conducted in two lots: AAB and AAE. The third and sixth sample in lot AAB are QC samples while the third sample in lot AAE is a QC sample.

3. A record will be maintained by the FQAC to associate the field sample with the various identification numbers used to analyze the field sample.

C. DATA MANAGEMENT ENTRIES

1. Data entered in the USATHAMA data management system will conform to the format in the Data Management User's Guide. A complete line of descriptors will be entered for each analyte or test in each sample.

2. A summary of the components in a line are given below. The numbers in parentheses are the columns in the format. The Data Management User's Guide should be consulted for abbreviations for possible entries.

   a. Installation (1-2). Enter the two letter abbreviation for the installation being surveyed. For example enter "AL" for Alabama AAP.

   b. Functional Area (3-4). Enter "SA".

   c. Type Data (5). Enter "C" for chemical.

   d. File (6-7). Enter the two letter abbreviation for the kind of sample. For example enter "AR" for air.

   e. Sample Date (8-12). Enter the 5-number Julian date when the sample was taken. The first two digits are the year; the last three digits are the day of the year. For example, "81032" represents 1 February 1981.

C. DATA MANAGEMENT ENTRIES (Cont)

f. Sampling Program (13-15). Enter the 3-character abbreviation for the type of program under which the sample was authorized. For example, enter "PRI" for preliminary survey, phase I. For QC samples, this field is left blank.

g. Site Type (16-19). Enter the 4-letter abbreviation for the site that was sampled. If the sample is a QC sample, instead of entering a site type:

(1) Enter "QCMB" for a QC method blank, i.e., an unspiked standard matrix introduced in the laboratory.

(2) Enter "QCSP" for a QC spike, i.e., a spike of a standard or natural matrix.

(3) Enter "QCFB" for a QC field blanks, i.e., an unspiked standard matrix introduced into the sample train in the field.

(4) Enter "QCDP" for an unspiked natural matrix duplicate.

h. Site Identification (20-29). Enter the 10 characters to identify the site type in more detail. Left justify the characters. Entries to correspond QC samples to actual samples are also made in these columns. This correlation is performed by entering the last four characters of the actual sample being referenced followed by

C. DATA MANAGEMENT ENTRIES (Cont)

"+" which is followed by the amount of the spike. For blanks, the amount of the spike would be "0.000." The amount of spike must be expressed so that an accurate description is obtained when the entry in columns 25-29 is read in conjunction with the measurement exponent (columns 63-65) and the measurement units (columns 66-69). For example, if QC Sample AAA003 in Section IX.B.2 were a duplicate of sample AAA001, the entry in colulmns 20-29 would be "A001 + 0.000." For QC samples (i.e., standard matrix samples) which cannot be correlated to natural samples, the QC sample will be related to itself. For example, if sample AAA003 were a method blank, the entry in columns 20-29 would be "A003 + 0.000."

i. Sample Depth (30-35). Enter 4 numbers to indicate depth of sampling in centimeters. This field may be left blank for QC samples.

j. Sampling Technique (34). Enter one character abbreviation to identify the sampling technique. This field may be left blank for QC samples.

k. Analysis Date (35-39). Enter the 5-number Julian date when analysis was made. The first 2 digits indicate the year; the last 3 digits indicate the day of the year.

C. DATA MANAGEMENT ENTRIES (Cont)

l. Laboratory (40-41). Enter the 2-letter abbreviation for the laboratory conducting the analysis. For example, enter "AE" for Aetna Technical Services Inc.

m. Sample Number (42-47). Enter the 6-character number assigned to the sample as discussed in Section IX.B.

n. Test Name (48-53). Enter the 6-character abbreviation for the parameter measured. For example, "2N3C" is entered for 3-methyl-2-nitrophenol. The User's Guide is listed alphabetically for both compounds and codes. Unidentifiable compounds found during screening may be entered as "UNKXXX" where "XXX" represents the number assigned by the field laboratory (001 to 999). Each unknown compound at an installation will have a unique code so that, when a compound is observed in different samples, the code will indicate that the same compound is being observed. Identified compounds for which no code exists will be submitted to the USATHAMA Analytical Branch for code assignment.

o. Test Method Number (54-55). Enter the 2-character designation assigned to the analytical method by the Analytical Branch.

p. Measurement Boolean (56-57). Enter the 2-character abbreviation to indicate that the measurement is less than detection limits,

greater than a certain value, or is qualitative. These columns may be left blank if they do not apply.

q. Measurement Mantissa (58-62). Enter the 5 characters (4 digits plus a decimal) to indicate the mantissa (in scientific notation) of the best estimate of the "true" value. Corrections to found values will have already been made to obtain this value. The decimal will appear in column 59. This field is left blank for qualitative analyses. Only one significant figure will be entered for semi-quantitative analyses.

r. Measurement Exponent (63-65). Enter 3 characters (+ or - sign plus 2 digits) to indicate the exponent to the base 10. This may be left blank for qualitative analyses.

s. Measurement Units (66-69). Enter the 4-letter abbreviation to indicate the units of measure. This field may be left blank for qualitative analyses reported as positive or negative.

(1) UGL - micrograms per liter will be used to report concentrations in liquids.

(2) UGG - micrograms per gram will be used to report concentrations in solids.

C. DATA MANAGEMENT ENTRIES (Cont)

(3) UGC2 - micrograms per square centimeter will be used to report concentrations on surfaces.

(4) MGM3 - milligrams per cubic meter will be used to report concentrations in air.

(5) "S" will be used in column 69 when the measurement is based on an internal or surrogate standard. Columns 66-68 will still contain abbreviations for the measurement units. For example, a concentration which is air based on an internal standard will indicate measurement units as "MGMS."

t. Accuracy (70-73). Enter 4 characters (3 digits plus a decimal) to represent the slope of the least squares regression line of found versus target values for spiked natural samples obtained on the date of analysis. This field will be blank for qualitative analyses. For semi-quantitative analyses in which estimates of concentration are based on internal standard, the three digits will be "000."

u. Precision (74-74). Enter 4 characters (3 digits plus a decimal) to represent the standard error of the estimate of the least squares regression line of found versus target values for spiked natural samples obtained on the date of analysis. Exponents and measurement units will be the same as that for the measurement

C. DATA MANAGEMENT ENTRIES (Cont)

mantissa. For qualitative analyses, the field will be left blank. For semi-quantitative analyses, "999." will be entered.

v. Instrument (78-79). Enter a 2-number code for the laboratory instrument to distinguish between same types within a laboratory. Codes are assigned by the Field Laboratory.

w. Analyst (80-82). Enter 3 letters to represent the initials of the individual responsible for the measurement.

X. STATISTICAL ANALYSIS OF DATA

X. STATISTICAL ANALYSIS OF DATA

A. FOUND CONCENTRATION:

1. Instrument calibration standards to cover the range of anticipated concentrations are prepared. These calibration standards are introduced to the instrument to obtain responses for the various concentrations.

2. An instrument calibration curve is constructed by plotting the response versus the calibration standard concentration and determining the best fit regression curve for the data. A measure of the linearity of the responses is the correlation coeffcient, Rxy.

3. The found concentration from the analysis of a sample is obtained by entering the instrument calibration curve with the sample response and reading the corresponding concentration. The concentration read from the calibration curve must be modified to reflect the concentration in the original matrix assuming 100% recovery through the analytical method. The resultant concentration is the found concentration.

B. DETECTION LIMIT:

1. Before any analytical system is employed in a survey, sufficient spikes and blanks will be run to statistically establish the lowest concentration which may be distinguished from zero. For USATHAMA programs, the detection limits will be determined by using the USATHAMA detection limit program with 90% confidence limits. Data for this determination will be from spiked standard samples. The lowest calculated concentration will be reported as the detection limit of the method provided that at least one of the spike (target) concentrations is below the calculated detection limit. Otherwise, the lowest spike concentration is the minimum level that can be reported as the detection limit. The highest spike concentration will represent the upper limit of reportable data.

2. If the calculated detection limit is higher than the lowest tested spike concentration and is higher than desired for the study, the detection limit is recalculated after discarding the data for the highest target concentration. Detection limits may be recalculated after successively discarding one concentration level at a time in decreasing order of concentration levels until a minimum detection is obtained. At least three positive target levels must be used in calculating the detection limit, and in no case will the reported detection limit be less than the lowest tested concentration or higher than the highest tested concentration used to calculate the detection limit.

B. DETECTION LIMIT (Cont)

3. The detection limit is derived from the assumptions that the relationship between the found concentration and target concentration is linear, that the variance about the least squares linear regression line is homogeneous over the tested concentration range, and that the distribution of found concentrations for a given target concentration is a normal distribution.

a. Based on these assumptions, the least squares linear regression line of the form,

$$Y = Y_0 + bx$$

is determined, where:

Y_0 = Y axis (found concentration) intercept

b = slope of the line, and

x = target concentration.

b. A measure of the linearity of the data is the correlation coefficient, Rxy.

$$R_{xy} = \frac{N\Sigma XY - (\Sigma X)(\Sigma Y)}{\sqrt{(N\Sigma X^2 - (\Sigma X)^2)(N\Sigma Y^2 - (\Sigma Y)^2)}}$$

where:

N = Number of target concentrations (multiply by 2 if duplicates are run)

X = Target value

Y = Found value

B. DETECTION LIMIT (Cont)

c. The confidence limits about the regression line are given by:

$$y = y_o + bx + S_{y.x}\, t \left[1 + \frac{1}{N} + \frac{(x-\bar{x})^2}{\Sigma(x-\bar{x})^2}\right]^{\frac{1}{2}}$$

for the upper confidence limit and

$$y = y_o + bx - S_{y.x}\, t \left[1 + \frac{1}{N} + \frac{(x-\bar{x})^2}{\Sigma(x-\bar{x})^2}\right]^{\frac{1}{2}}$$

for the lower confidence limit where

$$S_{y.x} = \left[\frac{\Sigma\{y_i - (\bar{y} + b(x_i - \bar{x}))\}^2}{N - 2}\right]^{\frac{1}{2}}$$

t = student's t for P = 0.05 and N-2 degrees of freedom,

N = number of target concentrations (multiply by 2 if duplicates are run),

$\bar{x}$ = the average of all target concentrations,

and $\bar{y}$ = the average of all found concentrations.

B. DETECTION LIMIT (Cont)

d. The detection limit, X_d, is the value of X corresponding to a point on the lower confidence limit curve where the value of Y equals the value of Y on the upper confidence limit curve at X = 0.

C. ACCURACY:

1. The slope, b, of the least squares regression line of a plot of found versus target concentrations is a measure of the accuracy of the method. The slope should be plus one (+1.0) for 100% recovery over the complete analytical method. Experimental values may deviate from this expected value.

2. Data from the analyses of standard samples will be used to determine the accuracy of an analytical method for methods certification or methods development. These data should provide an optimistic estimate of the accuracy of a method since interferences found in natural samples will be absent.

3. Estimates of accuracy are not required for qualitative analyses.

D. PRECISION:

1. The standard error of the estimate ($S_{y.x}$) for the least squares regression line of found versus target concentrations is a measure of the precision of the analytical method. See Section X.B.3.c.

2. Data from the analyses of standard samples will be used to determine the precision of the method. These data should provide an optimistic estimate of the precision of a method since variations due to interferences in natural samples should be absent.

3. Estimates of precision are not required for qualitative and semi-quantitative analyses.

E. CHARACTERIZATION OF ANALYTICAL METHODS:

1. When analytical methods are developed or a laboratory is to be certified to perform the method, data to characterize the method or to demonstrate a laboratory's ability to perform the method must be submitted to the USATHAMA Analytical Branch for review.

2. These data will include estimates of the standard deviation, percent inaccuracy, and percent imprecision.

   a. The standard deviation, S, will be calculated at each target concentration according to:

$$S = \left[\frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n - 1} \right]^{\frac{1}{2}}$$

   where X_i = the ith found concentration,

   n = total number of X values, and

   Σ = summation from i - i to i = n.

   b. The percent inaccuracy will be calculated at each target concentration according to:

$$\text{percent inaccuracy} = \frac{\bar{x} - TC}{TC} \times 100$$

   where $\bar{x}$ = average found concentration at the particular TC

   and TC = target concentrations.

E. CHARACTERIZATION OF ANALYTICAL METHODS (Cont)

c. The percent imprecision will be calculated at each target concentration according to:

$$\text{percent imprecision} = \frac{s}{\bar{x}} \times 100$$

where s = standard deviation

and $\bar{x}$ = average found concentration at the particular target concentration.

3. Estimates of the standard deviation, percent inaccuracy, and percent imprecision are not required for qualitative and semi-quantitative analyses.

XI. INSTRUMENTATION

XI. INSTRUMENTATION

A. INSTRUMENT CALIBRATION MAINTENANCE:

1. Purpose.

This section establishes the procedure for maintaining the accuracy of instruments and measuring equipment used to conduct tests and analyses.

2. Scope.

The calibration policies and procedures set forth herein shall apply to all test and measuring equipment. All test and measuring instruments fall into two general categories: those which are calibrated prior to each use and those which are calibrated on a scheduled, periodic basis.

3. Records.

a. All equipment to be calibrated under this procedure shall have an assigned record number permanently affixed.

b. A label will be affixed to each instrument showing: description, manufacturer, model number, serial number, date of last calibration, by whom calibrated (signature), and due date of next

calibration. Calibration reports and compensation or correction figures shall be maintained with the instrument.

c. A written stepwise calibration procedure must be available for each piece of test and measurement equipment.

d. Any instrument which is not calibrated to within the manufacturer's original specifications must display a red warning tag to alert the analyst that the device carried only a "limited calibration."

4. Calibration Identification.

a. Instruments past due for calibration shall be immediately removed from service either physically or, if this is impractical, by tagging, sealing, labelling, or other means.

b. The labelling and recording system extends to calibration services performed by commercial laboratories. Certifications and reports furnished by them shall be filed and made a part of this system.

c. Equipment in "Calibrate Before Use" (CBU) status must be administratively sequestered to avoid accidental use.

A. INSTRUMENT CALIBRATION MAINTENANCE (Cont)

5. Calibration Standards.

a. All measurements or calibrations performed by or for the laboratory shall be traceable, directly or indirectly, through an unbroken chain of properly conducted calibrations (supported by reports or data sheets) to the National Bureau of Standards.

b. Reports must be up-to-date for each reference standard and each subordinate standard used for calibration and for measuring and test equipment. When calibration services are performed by a commercial laboratory on contract, copies of their reports and records showing traceability to the National Bureau of Standards should be immediately available.

6. Calibration Frequency Schedule.

a. At a minimum, calibration intervals for complex or sensitive laboratory instruments shall be those recommended by the respective manufacturers unless experience dictates a shorter interval.

b. When the manufacturer has not specified a calibration interval for his equipment, the interval shall be established by the

calibration group servicing the laboratory. Adherence to the schedule is mandatory.

c. All laboratory instruments shall be calibrated and checked by competent personnel. The fact that these checks may be scheduled and performed by an outside source does not exempt the laboratory from its responsibility for identifying, monitoring, and controlling calibration intervals and seeing that checks are made on time.

B. GUIDELINES FOR MAINTAINING CONTROL OF SPECIFIC ANALYSES

1. Spectrophotometry (other than atomic absorption):

a. The important sources of systematic error in spectrophotometry of solutions have been summarized in Table 1. As used in the table, a positive error is one for which the apparent absorbance is greater than the true absorbance. The cited variables should be among those held sufficiently constant to ensure the continued applicability of confidence limits generated during the test and evaluation of the analysis.

Table 1

Systematic Error Sources in Spectrophotometry[3]

	A/A Range (Parts Per Thousand)
Solution temperature	-2 to +2
Solute apparent specific value	-1 to 0
Buoyancy correction	+0.2 to +1
Cell path-length	-10 to +10
Cell orientation	0 to +1
Multiple reflections	+0.5 to +3
Fine slit-width	-1 to 0
Stray radiation	-1 to 0
Wavelength offset	-1 to 0

b. It should be kept in mind that any substance which absorbs at the wavelength of interest may be present as an interference.

B. GUIDELINES FOR MAINTAINING CONTROL OF SPECIFIC ANALYSES (Cont)

2. Gas Chromatography/Liquid Chromatography:

a. Before use, gas chromatographic/liquid chromatographic systems must be checked for leaks. Flows through the column and detector must be optimized. The detector itself must be optimized according to the manufacturer's instructions.

b. For methods not utilizing an internal standard, a 10 µl syringe is used for injections of 2 to 7 µl, a 5 µl syringe is used from 0.7 to 2 µl, and 1 µl syringe is used from 0.1 to 0.7 µl.

B. GUIDELINES FOR MAINTAINING CONTROL OF SPECIFIC ANALYSES (Cont)

3. Atomic Absorption (AA) Spectrometry:

a. In atomic absorption, a number of variables must be held constant before the system is in statistical control. These variables include instrument warm-up, burner alignment, gas flow, lamp intensity, slit width, wavelength, matrix effects, aspiration time and aspiration rate.

b. Procedures will include a minimum warm-up period of 30 minutes. The hollow cathode tube will be aligned to produce the maximum emitted light to the detector. In flameless AA, the inert gas flow inside the furnace must be optimized to ensure maximum sensitivity.

c. For routine sample concentrations at levels greater than the highest standard of the analytical method, a secondary absorption line should be used in lieu of dilution.

d. The digital readout values obtained for the standard curve of each element should fall within a specified range. If readings are excessively low, the operator should check gas flows, burner or cell alignment, wavelength, slit width, photomultiplier voltage, and lamp intensity prior to analysis.

B. GUIDELINES FOR MAINTAINING CONTROL OF SPECIFIC ANALYSES (Cont)

e. If large amounts of dissolved salts are present in the solution to be analyzed, the nebulizer will not handle the solution in the same manner as it will a solution with small quantities of dissolved salts. Such an interference should be accounted for by adding a salt to the standards or by matching the density of the samples and standards.

f. Burner heads, nebulizers, quartz cells, and reduction flasks should be cleaned according to manufacturer's instructions whenever excessive electronic noise is apparent or whenever indicated by visual inspection. Tygon tubing should be replaced when deterioration is apparent. Optical lenses should be cleaned on a periodic basis.

B. GUIDELINES FOR MAINTAINING CONTROL OF SPECIFIC ANALYSES (Cont)

4. Technicon Autoanalyzers:

a. The pump tubes of each instrument shall be inspected before every day's run and replaced after each 40 hours of operation unless sooner replacement is dictated by deterioration of the tubes.

b. The temperature of the instrument room and reagents should be sufficiently controlled to maintain instrument stability.

5. Gas Chromatography/Mass Spectrometry:

a. A sample of decafluorotriphenylphosphine (DFTPP) is injected and the spectrum is checked for the following criteria[4]:

Mass	
51	30-36% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	1% of mass 198
441	Less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

B. GUIDELINES FOR MAINTAINING CONTROL OF SPECIFIC ANALYSES (Cont)

b. The identification of a compound by GC/MS will be the responsibility of the operator.

c. Hard copies of the reference and sample spectra of each identification will be included in the technical reports to USATHAMA.

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GLOSSARY

Analyte - Chemical component to be analyzed.

Calibration Standard - Solutions used in correlating instrument responses to analyte concentrations. See Section VIII.B.1.

Control Samples - Samples that are introduced into a train of actual samples as a monitor on the performance of the analytical system.

Deuterated Surrogate Standard - A surrogate standard containing deuterium.

Detection Limit - The lowest concentration that can be differentiated from zero, with a 90 percent confidence limit.

Duplicate Sample - Identical samples that are carried through the entire analytical method.

Field Blank - Samples prepared in standard matrices to which no analyte of interest has been added. Introduced into the sample train in the field. Used to detect contamination introduced in the field and laboratory.

Found Concentration - Concentration based on instrumental response of the sample compared to the instrument calibration curve and calculated to reflect the concentration in the original matrix assuming 100% recovery through the analytical method. See Section X.A.3.

Method Blank - Samples prepared in standard matrices to which no analyte of interest has been added. Used to detect contamination introduced in the laboratory.

Negative Interference - A response, or lack thereof, indicating a less amount of analyte than actually present.

Positive Interference - A response indicating the presence of an analyte in greater amounts than actually present.

SARM - Standard Analytical Reference Material (see Appendix 3, page 3-1).

Spiked Sample - A sample into which a known quantity of analyte has been introduced.

Standard Sample - Samples prepared in standard matrices as defined in Section VII.E.3.

Surrogate Standard - A compound or species used in lieu of actual analytes of interest to monitor recoveries from various matrices and to provide reference points for quantitation. Surrogate standards are spiked into original matrices.

Target Concentration - Spiked concentration.

Testing Lot - The maximum number of samples, including control samples, that can be analyzed during a single time period (not to exceed one day) as determined by the time or equipment limiting step of the analysis.

APPENDIX 1

FORMAT FOR DOCUMENTATION OF ANALYTICAL METHODS

APPENDIX 1

FORMAT FOR DOCUMENTATION OF ANALYTICAL METHODS

1. Application: State analytes that can be analyzed by this method and media in which the analytes are contained (e.g., TNT in soil). The media should be the original matrices to be analyzed (e.g., soil, air, water, biological tissue, etc.) rather than intermediates in the procedure (e.g., bubbler from air sampling, extract from soil, etc.).

a. Tested Concentration Range. State concentration range in the original matrix that was tested for this validation (e.g., 1-10 mg/l in water, 5-100 mg/m^3 in air, etc.).

b. Sensitivity. Response (peak height, area, etc.) observed for absolute quantity of analyte (state quantity) observed at the detection limit (e.g., 1500 area units for 40 picograms).

c. Detection Limit. Limit of detection for complete analytical method, determined from precision and accuracy data generated from spiked standard samples (standard water, soil, etc.) and calculated according to USATHAMA detection limit program, expressed in terms of concentration in original medium (soil, water, etc.).

d. Interferences. State any observed interferences or any interferences anticipated based on the method of analysis.

e. Analysis Rate. State the estimated number of samples that can be analyzed by this method in a 8-hour day after instrument calibration.

2. Chemistry:

a. List Chemical Abstracts Service registry number of analyte(s).

b. Describe in detail any chemical reactions involved in the analytical method (such as conversion of organic nitrogen to ammonia followed by conversion to ammonium chloride in hydrochloric acid).

3. Apparatus:

a. Instrumentation. List makes and models of instruments as well as specific characteristics (such as detectors).

b. Parameters. List operating parameters of instruments as well as chromatography columns.

c. Hardware/Glassware. List miscellaneous equipment. Include sources for specialty or trademarked items.

d. Chemicals. List chemicals necessary to perform method. State sources of analytical reference materials.

4. Standards:

   a. Calibration Standards. Describe, in detail, the step-by-step procedure for preparing instrument calibration standards to include proper storage and shelf life. Indicate concentrations of calibration standards.

   b. Control Spikes. Describe, in detail, the step-by-step procedure for preparing spikes of control samples.

5. Procedure: Describe, in detail, the step-by-step procedure for analyzing control and actual samples as well as instrument calibration procedures. If a published procedure contains the necessary detail and is used exactly as written, reference may be made to the publication.

6. Calculations: Describe, in detail, the manner by which the concentrations in the original matrix are calculated from the responses obtained in the analysis. Include instructions for constructing necessary graphs and formulas for calculating concentrations.

7. References: List any references used as a source for the procedures.

8. Data:

   a. Tabulate precision and accuracy data by indicating found concentrations (uncorrected) by day for each target concentration using the format below. Indicate the actual target concentration.

RUNS 1 2 3 4
COMPILATION OF TARGET CONC. VS FOUND CONC

Target Conc UG/L	Day 1 Found Conc UG/L	Day 2 Found Conc UG/L	Day 3 Found Conc UG/L	Day 4 Found Conc UG/L

b. Tabulate average found value, standard deviation, percent imprecision, and percent inaccuracy for each target value by using the following format:

c. Plot the found concentration versus the target concentration (include linear regression, confidence bounds, and detection limit).

RUNS 1 2 3 4
STATISTICAL DATA USED TO DETERMINE PERCENT INACCURACY AND IMPRECISION

Mn Targt Con UG/L	Mn Found Conc UG/L	Standard Deviation	Mean Pct Inaccuracy	Imprecision
Means				

APPENDIX 2

EXAMPLE QC PLAN TABLE OF CONTENTS

APPENDIX 2

EXAMPLE OF QC PLAN TABLE OF CONTENTS

APPENDIX 3

CHECKLIST FOR LABORATORY ADHERENCE

CHECKLIST FOR LABORATORY ADHERENCE

TO

QUALITY ASSURANCE PROGRAM

FOR

US ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY

_____

EVALUATED LABORATORY

Field QC Coordinator _____

Laboratory Chief _____

Evaluator _____

Evaluation Date _____

Field QA Coordinator:	Yes	No
1. Has individual been appointed who will not be subordinate to or be in charge of any person having direct responsibility for analysis?	___	___
2. Have SARMs been requested from Central QA Laboratory?	___	___
3. Has FQAC ensured that all test and measuring equipment are properly calibrated?	___	___
4. Has a detailed local Quality Control Plan, specific to the USATHAMA program being supported, been submitted to USATHAMA for approval?	___	___
5. Is FQAC responsible for logging in of samples?	___	___
6. Is FQAC responsible for introduction of control samples/ blind samples?	___	___
7. Does FQAC establish testing lots?	___	___
8. Does FQAC maintain records of qualifications of analysts?	___	___
9. Does FQAC approve all data before data are reported?	___	___

REMARKS.

Field QA Coordinator: (Cont)	Yes	No
10. Does FQAC have, on hand, control charts and supporting data to demonstrate that the systems which produce data are in control?	___	___
11. Does FQAC maintain a vigil over the entire laboratory operation to detect conditions which might indirectly jeopardize controls of various analytical systems?	___	___
12. Does FQAC ensure that subsampling and other handling procedures are consistent with the type of sample received?	___	___
13. Does FQAC oversee the quality of purchased laboratory materials?	___	___
14. Does FQAC have resources to function effectively in accordance with the intent of the plan?	___	___

REMARKS.

Analytical Systems Controls:	Yes	No
Sampling.		
15. Are the procedures for sampling water for volatile compounds being followed?	___	___
16. Are the procedures for sampling groundwater monitoring wells being followed?	___	___
17. Are the procedures for sampling water supply wells being followed?	___	___
18. Are the procedures for taking air samples being followed?	___	___
19. Are the correct sample containers being used for the type of sample collected?	___	___
20. Are sample containers cleaned as required by the plan?	___	___
21. Are samples preserved and stored according to approved procedures?	___	___

REMARKS.

Sample Management:	Yes	No
22. Are control samples (duplicates, spikes, blanks) introduced into the sample flow in an inconspicuous fashion?	___	___
23. Are the control samples introduced in such manner to insure that the QC samples are included within each lot?	___	___
24. Are numbers being assigned to all incoming samples (including QC samples) according to the format in the Data Management User's Guide?	___	___
Sample Preparation:		
25. Are appropriate water samples filtered through a 0.45 micron filter?	___	___
26. Are soil samples air dried before any portion is taken for analysis?	___	___
27. Are soil samples sieved in such a manner that no more than an insignificant percentage of the total sample surface area are retained on the sieve?	___	___
28. Is subsampling accomplished with the aid of a riffle or quartering?	___	___
29. Are moisture determinations run according to ASTM D2216-71?	___	___

REMARKS.

Standards:	Yes	No
30. Are the reference materials used in the preparation of standard samples supplied by Central QA Lab and stored at or below 4°C?	___	___
31. Are organic standard samples prepared by adding analyte(s) of interest to standard water?	___	___
32. Are inorganic standards prepared by adding analyte(s) of interest to deionized water?	___	___
33. Are standard soil samples prepared in a soil representative of the soil to be analyzed?	___	___

REMARKS.

Analytical Methods:	Yes	No
34. Have methods to be used been approved by the USATHAMA Analytical Branch?	___	___
35. For published methods of analysis, are data available to demonstrate the precision and accuracy of the method?	___	___
36. Are the methods utilized in a manner for which they were intended?	___	___
37. For analyses for which no reliable methods exist, has the method development been pursued according to the steps for development of a method as outlined in USATHAMA QA Program?	___	___
38. Are the developed procedures documented according to the format in the USATHAMA QA Program?	___	___
39. Have precision and accuracy data been generated for the method?	___	___

REMARKS.

Control Charts:	Yes	No
40. Are control charts kept for each operation?	___	___
41. Are precision control charts prepared as described in the USATHAMA QA Program?	___	___
42. Are accuracy control charts prepared as described in the USATHAMA QC Program?	___	___
43. Does laboratory stop analyses when an analytical system goes out of control?	___	___
44. Are the out-of-control situation and the corrective actions used in getting systems back in control documented?	___	___

REMARKS.

Laboratory Certification:	Yes	No
45. Are analysts required to qualify with the specific analytes before running an analysis?	___	___
46. Is proficiency demonstrated for each analyte to be analyzed prior to conducting analysis of natural samples?	___	___
47. Is a log kept on those individuals qualified to run an analysis?	___	___
48. Are the procedures for certification for qualitative and quantitative analysis according to the USATHAMA QA Program being followed?	___	___
49. Has the documentation on the analytical certification testing been submitted to the USATHAMA Analytical Branch for review?	___	___

REMARKS.

Analysis of Samples:	Yes	No
50. Are all methods readily available in approved written format?	___	___
51. Have all analytical methods been reviewed and approved by the USATHAMA Analytical Branch?	___	___
52. Have data to support the limitations of the method (precision, accuracy, and detection limits) been submitted?	___	___
53. Are all standards prepared from Standard Analytical Reference Materials?	___	___
54. Are percent recoveries determined on control soils representing each type of soil to be encountered?	___	___

REMARKS.

Analysis of Samples: (Cont)	Yes	No
55. If a column is not used for percent recovery studies, is the "spike" allowed to remain in contact with the soil for a minimum of one hour before extraction?	___	___
56. If a column is not used for percent recovery studies, is the analyte dissolved in a minimum volume of solvent sufficient to completely wet the sample?	___	___
57. If a column is used for extraction, is the analyte introduced in a minimum quantity of solvent?	___	___
58. Are samples concentrated using Kuderna-Danish evaporative concentrations?	___	___
59. Is the correct syringe used for the volume of sample injected?	___	___
60. Are operators required to qualify for GC operations by a documented test?	___	___
61. Is the sensitivity of the GC/MS plotted on a control chart?	___	___

REMARKS.

Qualitative Analysis:	Yes	No
62. Has detection limit of the total method been determined according to USATHAMA QA Program?	___	___
63. Is instrument calibration (on each day in which analyses are performed) being accomplished as described in the QA Program?	___	___
64. Are results reported in terms of concentration in the original matrix (corrected for recoveries, systematic errors, etc.)?	___	___
65. Is a control sample included with each lot of natural samples?	___	___
66. Are the results being reported according to the conditions as described in the USATHAMA QA Program?	___	___

REMARKS.

Quantitative Analysis:	Yes	No
67. Have all analytical methods been documented according to the format in the USATHAMA QA Program and reviewed and approved by the USATHAMA Analytical Branch?		
68. Has initial calibration been accomplished according to the USATHAMA QA Plan?	___	___
69. Are a minimum of three instrument calibration standards run before and after each day's analyses?	___	___
70. Is at least one control sample (the working value of which has been established and that will be run through the entire test procedure) included with each lot of samples?	___	___
71. Are the data generated from the daily control samples being used to update control charts, refine the detection limit of the method as well as the estimates of precision and accuracy?	___	___
72. Are the estimates of concentration level in quality control and actual samples reported according to the guidelines in the program tasking and the Data Management User's Guide?	___	___

REMARKS.

Statistics:	Yes	No
73. Are found concentrations determined as described in the USATHAMA QA Program?	___	___
74. Are detection limits determined as described in the USATHAMA QA Program?	___	___
75. Are accuracy and precision determined according to the USATHAMA QA Program?	___	___
76. Are documented calculations available for inspection?		
77. Have the characterization of analytical methods been accomplished according to the USATHAMA QA Program?	___	___

REMARKS.

Data Management:	Yes	No
78. Are samples logged-in according to the USATHAMA QA Program?	___	___
79. Have the appropriate sample identification numbers been assigned?	___	___
80. Have data been entered into the USATHAMA Data Management System according to the format in the Data Management User's Guide?	___	___

REMARKS.

Calibration:	Yes	No
81. Does equipment contain inventory control numbers?	___	___
82. Is there a label affixed to each piece of equipment showing when calibration was performed and when it is next due?	___	___
83. Are detailed calibration procedures available?	___	___
84. Are warnings posted on instruments when calibration is not to manufacturer's original specifications?	___	___
85. Are instruments that are past due for calibration removed from service either physically or by tagging, etc.?	___	___
86. Is equipment that is to be calibrated before use clearly designated as such?	___	___
87. Are calibration standards traceable to NBS?	___	___
88. Is the calibration frequency scheduled at intervals recommended by instrument's manufacturer?	___	___

REMARKS.

SARMs/Interim Reference Materials	Yes	No
89. Is a local repository (4°C) maintained for the storage of SARMs?	___	___
90. Are SARMs (or interim reference materials) available for each analysis run by the laboratory?	___	___
If interim reference materials were obtained by the Field Laboratory, is the following information available for organics:		
91. Infrared spectrum?	___	___
92. MP, decomposition point, or BP?	___	___
93. NMR spectrum?	___	___
94. Elemental analysis?	___	___
95. GC analysis, LC analysis, and/or DSC analysis?	___	___
96. Has some of the material being utilized as an interim reference materials been retained for comparison with an approved SARM when received?	___	___

REMARKS.

General Laboratory Overview:	Yes	No
97. Is acceptable water available?	___	___
98. Are all solutions properly labeled?	___	___
99. Are facilities and instrumentation sufficient to perform the required analyses?	___	___
100. Are samples or standards containing the analytes of interest stored or used in an area other than the area where analytical systems are used for trace analysis?	___	___
101. Are chemical and reagents of sufficient quality so as not to compromise the analytical systems?	___	___
102. Is housekeeping commensurate with good analytical techniques?	___	___

REMARKS.

APPENDIX 4

RECOMMENDED PROCEDURE FOR THE STORING OF WATER SAMPLES

APPENDIX 4

RECOMMENDED PROCEDURES FOR THE STORING OF WATER SAMPLES

1. To ensure the integrity of water samples, steps must be taken to minimize contamination from the containers they are stored in. If the analyte(s) to be determined are organic in nature, the container should be made of amber glass. If the analyte(s) are inorganic, then the container should be plastic. When both organic and inorganic substances are expected to be present, duplicate samples, if at all possible, should be taken. The procedures for cleaning the glass and plastic containers and their caps are as follows:

a. Amber bottles.

(1) Soak bottles in detergent for one day.

(2) Scrub to remove deposits of foreign materials.

(3) Rinse with copious amounts of distilled water.

(4) Rinse with acetone.

(5) Rinse with methylene chloride (nanograde).

(6) Rinse with hexane (nanograde).

(7) Air dry.

(8) Heat to 200°C.

(9) Allow to cool.

(10) Cap with clean caps with teflon liners.

b. Plastic bottles.

(1) Rinse bottles and lids with 5% sodium hydroxide.

(2) Rinse with distilled water.

(3) Rinse with 5% ultrex nitric acid in deionized water.

(4) Rinse with deionized water.

(5) Drain and air dry.

c. Bottle caps.

(1) Remove paper liners from caps.

(2) Wash with detergent.

(3) Rinse with distilled water.

(4) Dry at 40°C.

d. Teflon liners (avoid contact with fingers).

(1) Wash with detergent.

(2) Rinse with distilled water.

(3) Rinse with acetone.

(4) Rinse with hexane (nanograde).

(5) Air dry.

Place liners in cleaned caps; heat to 40°C for two hours. Let cool in vacuum desiccator until used.

2. After the samples have been taken, they should be sent to the laboratory for analysis as expeditiously as possible in order to insure that the most reliable and accurate answers will be obtained as a result of the analysis. As a general rule, storage at low temperature is the best way to preserve most samples, although the length of time the sample can be held even at low temperatures varies with the analyte. Those samples being examined for organochlorine residues may be held up to a week at 2-4°C. Those intended for organophosphorus or carbamate analysis should be frozen immediately after taking the sample and should be extracted no more than four days after sampling. These samples should be extracted immediately (utilizing the procedure specified for the suspected analytes), and the extracts should be immediately sent to the laboratory for analysis. The bottles should be packaged for shipping in insulated containers that are constructed in a manner that insures that the bottles will arrive at the laboratory intact.

3. When the samples are received at the laboratory for analysis, there may be an appreciable time lapse between receipt of samples and actual analysis. The procedures summarized in the following table are to be utilized for the preservation and storage of the samples.

TABLE 1*

CONTAINERS, PRESERVATION, AND HOLDING TIMES

Measurement	Container	Preservative	Maximum Holding Time
Acidity	P	Cool, 4°C	14 days
Alkalinity	P	Cool, 4°C	14 days
Ammonia	P	Cool, 4°C H_2SO_4 to pH<2	28 days
Biochemical oxygen demand	P	Cool, 4°C	48 hours
Biochemical oxygen demand Carbonaceous	P	Cool, 4°C	48 hours
Bromide	P	None required	28 days
Chemical oxygen demand	P	Cool, 4°C H_2SO_4 to pH<2	28 days
Chloride	P	None required	28 days
Chlorine, total residual	P	Determine on site	2 hours
Color	P	Cool, 4°C	48 hours
Cyanide, total and amenable to chlorination	P	Cool, 4°C NaOH to pH>12 0.008% $Na_2S_2O_3$[f]	14 days
Dissolved oxygen			
Probe	G bottle & top	Determine on site	1 hour
Winkler	G bottle & top	Fix on site	8 hours
Fluoride	P	None required	28 days
Hardness	P	HNO_3 to pH<2	6 months
Hydrogen ion (pH)	P	Determine on site	2 hours
Kjeldahl and organic nitrogen	P	Cool, 4°C H_2SO_4 to pH<2	28 days
Metals[d]			
Chromium VI	P	Cool, 4°C	48 hours
Mercury	P	HNO_3 to pH<2 0.05% $K_2Cr_2O_7$	28 days
Metals except above	P	HNO_3 to pH<2	6 months
Nitrate	P	Cool, 4°C	48 hours
Nitrate-nitrite	P	Cool, 4°C H_2SO_4 to pH<2	28 days
Nitrite	P	Cool, 4°C	48 hours
Oil and Grease	G	Cool, 4°C H_2SO_4 to pH<2	28 days
Organic Carbon	G	Cool, 4°C H_2SO_4 to pH<2	28 days

TABLE 1*

CONTAINERS, PRESERVATION, AND HOLDING TIMES (Cont)

Measurement	Container	Preservative	Maximum Holding Time
Organic Compounds [e] Extractables (including phthalates, nitrosamines organochlorine pesticides, PCB's, nitroaromatics, isophorone, polynuclear aromatic hydrocarbons, haloethers, chlorinated hydrocarbons and TCDD)	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$ [f]	7 days (until extraction) 30 days (after extraction)
Extractables (phenols)	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$ [f]	7 days (until extraction) 30 days (after extraction)
Purgeables (halocarbons, aromatics, Acrolein, and Acrylonitrile)	G, teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$ [f]	14 days
Orthophosphate	P	Filter on site Cool, 4°C	48 hours
Pesticides	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$ [f]	7 days (until extraction) 30 days (after extraction)
Phenols	G	Cool, 4°C H_2SO_4 to pH<2	28 days
Phosphorus (elemental)	G	Cool, 4°C	48 hours
Phosphorus, total	P,G	Cool, 4°C H_2SO_4 to pH<2	28 hours
Residue, total	P	Cool, 4°C	14 days
Residue, filterable	P	Cool, 4°C	14 days
Residue, nonfilterable	P	Cool, 4°C	7 days
Residue, settleable	P	Cool, 4°C	7 days
Residue, volatile	P	Cool, 4°C	7 days
Silica	P	Cool, 4°C	28 days
Specific conductance	P	Cool, 4°C	28 days
Sulfate	P	Cool, 4°C	28 days
Sulfide	P	Cool, 4°C Zinc Acetate	28 days

TABLE 1*

CONTAINERS, PRESERVATION, AND HOLDING TIMES (Cont)

Measurement	Container	Preservative	Maximum Holding Time
Sulfite	P	Cool, 4°C	48 hours
Surfactants	P	Cool, 4°C	48 hours
Temperature	P	Determine on site	Immediately
Turbidity	P	Cool, 4°C	48 hours

a - Polyethylene (P) or Glass (G).
b - Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection. When use of an automatic sampler makes it impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.
c - Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples maybe held for longer periods only if the laboratory has data on file to show that the specific types of samples under study are stable for the longer time. Some samples may not be stable for the maximum time period given in the table. A laboratory is obligated to hold the sample for a shorter time if knowledge exists to show this is necessary to maintain sample integrity.
d - Samples should be filtered immediately on site before adding preservative for dissolved metals.
e - Guidance applies to samples to be analyzed, by GC, LC, or GC/MS for specific organic compounds.
f - This should only be used in the presence of residual chlorine.

(Compounds not found on Table 1 should be preserved at 4°C; storage: 1 week).

*Adapted from Federal Register, December 18, 1979. Volume 44, Number 244, pp. 75050-75052.

APPENDIX 5

DOCUMENTATION FOR PROPOSED METHODS DEVELOPMENT

APPENDIX 5

DOCUMENTATION FOR PROPOSED METHODS DEVELOPMENT

1. Organization submitting documentation.

2. Statement of the problem.

3. Description of the technical approach to include specific details on procedures, solvents, instrumentation, etc.

4. Estimate of resources required to include hours, funds, and schedule.

APPENDIX 6

SARM DEVELOPMENT

APPENDIX 6

SARM DEVELOPMENT

1. Due to the limited availability of reference materials for trace organic analyses from the NBS, USATHAMA has initiated a program for the development of Standard Analytical Reference Materials (SARMs) for use in its programs.

a. Candidate methods for high purity analyses are selected and evaluated by the SARM developer on a preliminary basis using known materials. Appropriate standards (traceable to NBS) are selected and procured. Sufficient analyses are run to document the random and systematic errors in the analyses. The most appropriate method of high purity analysis is selected for the evaluation of the analytical standards.

b. Raw materials are synthesized or procured and purified to greater than 98 mole percent. Purities above 98 mole percent can be conveniently and precisely determined in many cases by differential scanning calorimetry using the premelting technique. Wet analyses are used where required. Precision and accuracy data must be presented to support each high purity analysis used to guarantee a standard. Chromatographic analyses are used only to estimate impurities and thus support an analysis by difference. Chromatographic, spectrophotometric, and NMR examination are routinely used to ensure that each material of certified high purity is indeed the correct compound.

c. Each SARM must be subjected to an aggravated storage period to estimate its stability. Materials showing a propensity for decomposition must be repurified and stabilized if practical. Where not practical, an alternate standard may have to be selected. SARMs should emerge from aggravated storage with purities in excess of 98 mole percent.

(1) Criteria for test results. Results of the tests will be expressed as mole percent purity before and after the two weeks test. Unanticipated observations concerning the condition of the standard will be noted. Conditions under which the test is conducted will be fully documented in the reporting of results. If the purity of the standard does not fall below the 98 mole percent value and there are no conditions observed in the standard that would interfere with the analytical system, the standard will have successfully passed the test.

(2) Test procedure. Liquid SARMs are sealed in glass bottles with crimp type septum tops (solid SARMs are sealed in screw top bottles) under normal atmosphere and are subjected to temperatures of 70°C for a period of two weeks. These SARMs are then cooled and stored in a freezer until they can be analyzed. When a standard degrades below 98 mole percent, the cause is sought and special storage conditions will be developed. Special storage conditions might include dark glass containers, inert atmosphere, lowered temperature, or addition of a stabilizer. If a material is found to be too unstable for storage, a

new SARM may have to be selected. The analytical technique initially used to guarantee the purity of each SARM will be repeated after aggravated storage in order to detect degradation.

(3) Reports. The results of the testing will be submitted to the USATHAMA Analytical Branch. The Analytical Branch will review the suitability of each material and all its supporting data for adequacy as a SARM.

2. SARM Surveillance Program.

a. At six-month intervals, surveillance samples will be removed from the repository and reanalyzed by the original acceptance methods.

b. Purpose. The purpose of this surveillance program is to confirm the integrity of each SARM by scheduled analyses.

c. Conditions. All SARMs will be protected from UV radiation and stored in bulk at 0°C. SARMs which have been purchased in 98 mole percent purity will be stored in the manufacturer's container. Where possible, purified SARMs will be stored in glass stoppered flasks which have been sealed with Parafilm. Glass bottles with crimp type tops will be used where necessary (e.g., DIMP "creeps" around glass stoppers. Consequently, it would be sealed in these bottles). Air sensitive compounds will be stored under inert atmosphere. Hygroscopic compounds will be stored with desiccant in a sealed outer container.

d. Test Procedure. A specimen will be withdrawn (under the appropriate atmosphere) from each SARM at prescribed intervals. Purities of these specimens will be determined using the original acceptance tests.

e. Criteria for Surveillance. The standards must remain at least 98 mole percent pure through the surveillance program. If a SARM fails to meet this criterion, its use will be suspended immediately and all laboratories using it will be notified by the central repository by phone. Follow-up correspondence will be prepared by the Central Laboratory Quality Assurance Coordinator.

f. Program. The surveillance program for each SARM will begin when the material is purified and placed in the 0°C repository. If further purification is indicated by the aggravated storage phase, the surveillance period wil be reinitiated upon completion of the repurification. Thus, the aggravated storage will be carried out concommitantly with the first two weeks of the first surveillance cycle. Any required subsequent repurification of the SARM will reinitiate the surveillance program. Each surveillance cycle will last six months. The entire program will continue for two years for each SARM. At this time, aggravated storage will be repeated on a specimen of the original material or newly obtained material as availability and projected needs for the material at that time dictate. Materials which have been deleted from the surveys will be removed from the surveillance program at the convenience of USATHAMA.